Geological Evolution and Analysis of Confirmed or Suspected Gas Hydrate Localities

Volume 1. Blake-Bahama Outer Ridge- U.S. East Coast

By
J. Krason
W.I. Ridley

PREFACE

This document is Volume 1 of a series of reports entitled "Geological Evolution and Analysis of Confirmed or Suspected Gas Hydrate Localities." Volume 1 is an analysis of the "Blake-Bahama Outer Ridge - U.S. East Coast." This report presents a geological description of the Blake-Bahama Outer Ridge, including regional and local structural settings, geomorphology, geological history, stratigraphy, and physical properties. It provides the necessary regional and geological background for more in-depth research of the area. Detailed discussion of bottom simulating acoustic reflectors, sediment acoustic properties, distribution of hydrates within the sediments, and the relation of hydrate distribution to other features such as salt diapirism are is also included. The formation and stabilization of gas hydrates in sediments are considered in terms of phase relations, nucleation, and crystallization constraints, gas solubility, pore fluid chemistry, inorganic diagenesis, and sediment organic content. Together with a depositional analysis of the area, this report is a better understanding of the thermal evolution of the locality. It should lead to an assessment of the potential for thermogenic hydrocarbon generation.

Project Manager
Gas Hydrates

Acknowledgments

CONTENTS

ILLUSTRATIONS

TABLES

APPENDIX

BASIN ANALYSIS, FORMATION AND STABILITY OF GAS HYDRATES IN THE BLAKE - BAHAMA OUTER RIDGE

EXECUTIVE SUMMARY

Gas hydrates are clathrates in which gas molecules are trapped within cages of water molecules. The gas molecules stabilize the ice structure to temperatures and pressures outside the range of pure ice. Consequently, gas hydrates exist in nature in environments where pure ice is unstable. The offshore marine, subbottom environment is one such example. The impetus for current research is largely the potentially vast reservoirs of natural gas locked within or beneath gas hydrates, a resource as yet unassessed with regard to reserves or economic potential.

Twenty-four offshore sites have currently been identified, with varying degrees of confidence, as carrying gas hydrates. The present report is a site-specific study which evaluates the geological factors effecting gas hydrate stability in the region of the Blake - Bahama Outer Ridge.

The report presents a geological description of the Blake - Bahama Outer Ridge, including regional and local structural setting, geomorphology, geological history, stratigraphy, and physical properties. The occurrence of gas hydrates at the Blake - Bahama Outer Ridge is discussed in detail with regard to bottom simulating acoustic reflectors (BSRs), sediment acoustic properties, distribution of hydrates within the sediments, and the relation of gas hydrate distribution to salt diapirism. The formation and stabilization of gas hydrates in sediments are discussed in terms of phase relations, nucleation and crystallization constraints, gas solubility, pore fluid chemistry, inorganic diagenesis, and sediment organic content. A depositional analysis is discussed in order to understand the thermal evolution of the ridge and to assess the potential for thermogenic hydrocarbon generation.

This study concludes that the Blake - Bahama Outer Ridge developed an unusually high rate of sedimentation due to a complex interaction of the Gulf Stream and western boundary undercurrent. The high clastic flux was critical in providing anoxic sedimentation conditions that facilitated organic matter preservation. Bacterial processes within the sediment column produced methane which was subsequently incorporated into gas hydrates. The hydrates were stabilized to approximately 500 m subbottom depth in the hemipelagic sediments due to appropriate anoxic conditions, low bottom water temperature, and a heat flow gradient of 3.6°C/100 m. The acoustic bottom simulating reflector is a strong seismic return from the base of the hydrate zone due to the marked acoustic impedance contrast between hydrated and underlying gassy sediments.

The BSRs cover a minimum area of 31,000 km^2 and probably as much as 53,000 km^2. A gas hydrated zone 50 m thick would contain approximately 14 trillion cubic feet (TCF) of producible gas at the wellhead. A zone 400 m thick would contain approximately 66 TCF, assuming a disseminated type of deposit (Table 1).

The study also emphasizes the need for further investigation of potential offshore gas hydrate sites, particularly with regard to relating seismic information to the distribution of hydrated sediments.

TABLE 1. Summary Data of Basin Analysis, Formation and
Stability of Gas Hydrates in the Blake-Bahama Outer
Ridge, is located in the pocket at the end of the report.

INTRODUCTION

In 1981 the United States Department of Energy (DOE), through the Morgantown Energy Technology Center (METC), initiated a program of gas hydrate research. Part of this program involves an evaluation of the geological factors resulting in gas hydrate formation and stability in both onshore and offshore environments. To date, twenty-four offshore sites have been identified (Kvenvolden and McMenamin, 1980) which are considered, with varying degrees of confidence, to carry gas hydrates (Appendix). Consequently, DOE - METC mandated Geoexplorers International, Inc to study each site and provide a separate report. This report is therefore a site-specific study and discusses the region of the Blake - Bahama Outer Ridge, designated site No. 1 by DOE - METC (Appendix).

Specific purposes of the report are as follows:

1. To collate literature pertinent to the formation and stabilization of gas hydrates at the Blake - Bahama Outer Ridge site covering such general areas as geology, geophysics and geochemistry.

2. To provide a geological description of the site through an analysis of available data.

3. To assemble a data base of information which may be retrieved for future studies and to identify pertinent data gaps.

4. To provide a depositional analysis whereby the formation and stabilization of hydrates may be considered within the framework of sedimentation rate, lithology, temperature, pressure, and fluid chemistry.

5. To identify site-specific gas hydrate stability factors for comparison to stability factors for other sites.

6. To provide a framework of site reports from which a final synthesis may be prepared in order to recognize the important general factors that are critical in the potential resources assessment and can influence gas hydrate stability in the offshore, subbottom environment.

Gas Hydrates in Nature

Gas hydrates are clathrates in which gas molecules are trapped within a cage of water ice molecules. The gas molecules stabilize the ice structure to temperatures and pressures outside the range of pure ice. Consequently, gas hydrates exist in nature in environments where pure ice may be unstable. The offshore marine, subbottom environment is one example.

From a historic perspective, gas hydrates were first discovered in 1810 when Davy synthesized chlorine hydrate (Davy, 1811). Their occurrence in nature was first predicted by glaciologists who correctly determined that nitrogen hydrate should be stabilized in the deeper parts of massive glaciers. Remote spectroscopic observations indicate that gas hydrates may be present on the surfaces of the outer solar system planets and their satellites because of their low ambient temperatures and appropriate gaseous compositions (Miller, 1974).

Gas hydrates may occur in pipelines transporting natural gas at high pressure under circumstances where the natural gas is wet and the temperatures are sufficiently low (Hammerschmidt, 1934). The growth of hydrates, particularly methane hydrate, leads to pipeline clogging and a significant reduction in gas flow rates. Such a detrimental effect led to an intensive study of hydrate stability in the 1960s and 1970s, particularly in Russia (Makogon, 1978), towards preventing hydrate growth. This body of chemical data forms the basis for our present knowledge of the stability of a wide variety of gas hydrates.

The hydrates of methane, ethane, and propane were synthesized by Villard (1888), and a great deal of research has focused on the pressure - temperature stability of these hydrates (Kobayashi and Katz, 1949; Deaton and Frost, 1940; Frost and Deaton, 1946; and many others). In nature, hydrates more complex than iso-butane are not observed because of structural limitations; in natural gas systems the dominant hydrate is always methane hydrate.

Natural gas hydrates occur extensively in permafrost zones where a zone of permanently frozen ground exists to various depths. Such occurrences have been well documented from the arctic regions of Siberia (Makogon, 1965, 1978), Canada (Judge, 1984) and Alaska (Collett, 1984; Kvenvolden, 1984). In these environments the natural gas hydrates occur in porous reservoir rocks and are stabilized partly because of the constantly low surface temperature. They are geographically restricted to high latitudes and exist at relatively low pressures.

Natural gas hydrates have also been observed and predicted beneath the offshore continental margins where the bottom water temperatures approach 0°C along the continental slopes and rises. The higher temperatures and lower pressures along the shallow continental shelves preclude stabilization of gas hydrates in the underlying sediments. Consequently, hydrates have only been directly and indirectly identified beneath the rise and slope environments. The marine deep-water environment is hostile for collection and identification of in situ gas hydrates, given current technology. Therefore, samples of offshore gas hydrates are quite rare. The identification of hydrates in this environment frequently relies on more indirect geological, geophysical, and geochemical data.

As briefly described above, original interest in natural gas hydrates was focused on preventing their formation in high pressure pipelines. Subsequently, research expanded to evaluate more accurately the factors determining hydrate stability in geological environments. The impetus for current research is the potential for vast reservoirs of natural gas locked within or beneath gas hydrates, a resource as yet unexplored. Natural gas hydrate deposits present a significant technical challenge regarding their exploitation, particularly in the deep sea environment, if they are to be a future, economically viable source of hydrocarbon gas. A challenge of similar magnitude confronts the

geologists in attempting to identify and evaluate geological factors which influence hydrate stability. Such factors need to be considered not only as variables in developing hydrate production technology but also in future exploration programs that seek to discover new hydrate localities, assess the hydrate resource, and evaluate the economic potential.

The evaluation of geological factors which influence hydrate stability must ultimately depend upon an understanding of the physico-chemical parameters which determine hydrate formation and stability. Such data are available in the literature, so the task becomes one of interpreting the data in a geological context. This, in turn, requires a knowledge of the geological evolution of a hydrate-bearing site, particularly with regard to geochemistry and petrophysics.

Although many gases and liquids may form hydrates, only the hydrates of light hydrocarbons (methane, ethane, propane, butane), nitrogen, carbon dioxide, and hydrogen sulfide are important in nature from a resource view-point. Of these, methane hydrate dominates all natural systems examined to date, and most estimates of hydrocarbon hydrate stability rely upon the stability field of methane hydrate as basic data. Nonetheless, it would be premature to conclude that insignificant resources of other hydrocarbon hydrates and inorganic hydrates exist in nature in the absence of more detailed knowledge of hydrate occurrences and their volumetric extents.

The dominance of methane hydrate in natural gas systems reflects the biological and/or thermal origin of the gaseous hydrate-forming component, as discussed below. With an increased contribution of thermogenic gas, the probability increases of stabilizing hydrocarbon hydrates other than methane. Many natural gas seeps, as well as a body of data on microseepage, clearly demonstrate that thermally generated natural gas contains significant C_2 - C_4 hydrocarbon components. In addition, under appropriate conditions the distribution coefficients (hydrate/gas) strongly favor the hydrate phase for these species, so that C_2 - C_4 hydrates are preferentially developed, even in the presence of a dominant methane component. However, given our present level of knowledge, it appears that methane hydrate dominates systems involving biogenic or thermogenic gas.

PART I

GEOLOGY OF THE BLAKE - BAHAMA OUTER RIDGE

Regional Structural Setting

The Blake - Bahama Outer Ridge lies within the eastern United States Continental Margin, which stretches from Florida to Maine. Largely through the marine investigations of the U.S. Geological Survey (USGS) and Lamont-Doherty Geological Observatory (LDGO) this margin has been extensively studied and its regional tectonic evolution is well understood. In the framework of plate tectonics it is frequently cited as the classic "passive" continental margin (Bally, 1981).

The major tectonic features of the margin are shown in Figure 1, based on maps presented by Klitgord and Behrendt (1979), Grow (1981), and Grow et al. (1983). This map, in turn, is partly based upon studies by Schlee et al. (1981), Dillon (1979), Grow et al., (1979), Sheridan et al. (1979), Klitgord and Grow (1980), Schlee (1981), Grow (1981), Grow and Sheridan (1981, 1982), and Hutchinson et al. (1983).

The tectonic features developed during and after the Triassic rifting of North America from North Africa. Half grabens filled with fluvial and other nonmarine sediments outcrop onshore, e.g. Newark Basin, and have been identified on seismic section beneath the eastern U.S. Continental Margin (see Manspeizer, 1981, for a comprehensive review). Such sediments are frequently referred to pre-rift or syn-rift tectonism and deposition and underlie a regional post-rift unconformity. Above the unconformity are thick sequences of Mesozoic and Cenozoic sediments which generally have their thickest development in a series of elongate offshore basins whose long axes roughly parallel the present coastline. The major basins included in this category are: Scotian, Georges Bank, Baltimore Canyon Trough, Carolina Trough, and Blake Plateau (Figure 1). They developed under and seaward of the present continental shelf edge and are not related, from a depositional viewpoint, to the present topographic expression of shelf, slope, and rise. Structural interpretation of numerous seismic sections, e.g. Grow et al. (1983), indicates the presence of a buried Jurassic paleoshelf edge about 100 km seaward of the present shelf edge. The paleoshelf controlled sediment distribution throughout much of the Mesozoic.

The deeper continental margin structure can be estimated from seismic, gravity, and magnetic data, principally collected by USGS and LDGO. A distinct magnetic anomaly, termed the east coast magnetic anomaly (ECMA), traverses the continental margin. Keen (1969) has suggested that the ECMA reflects an edge effect between strongly magnetized oceanic crust beneath the
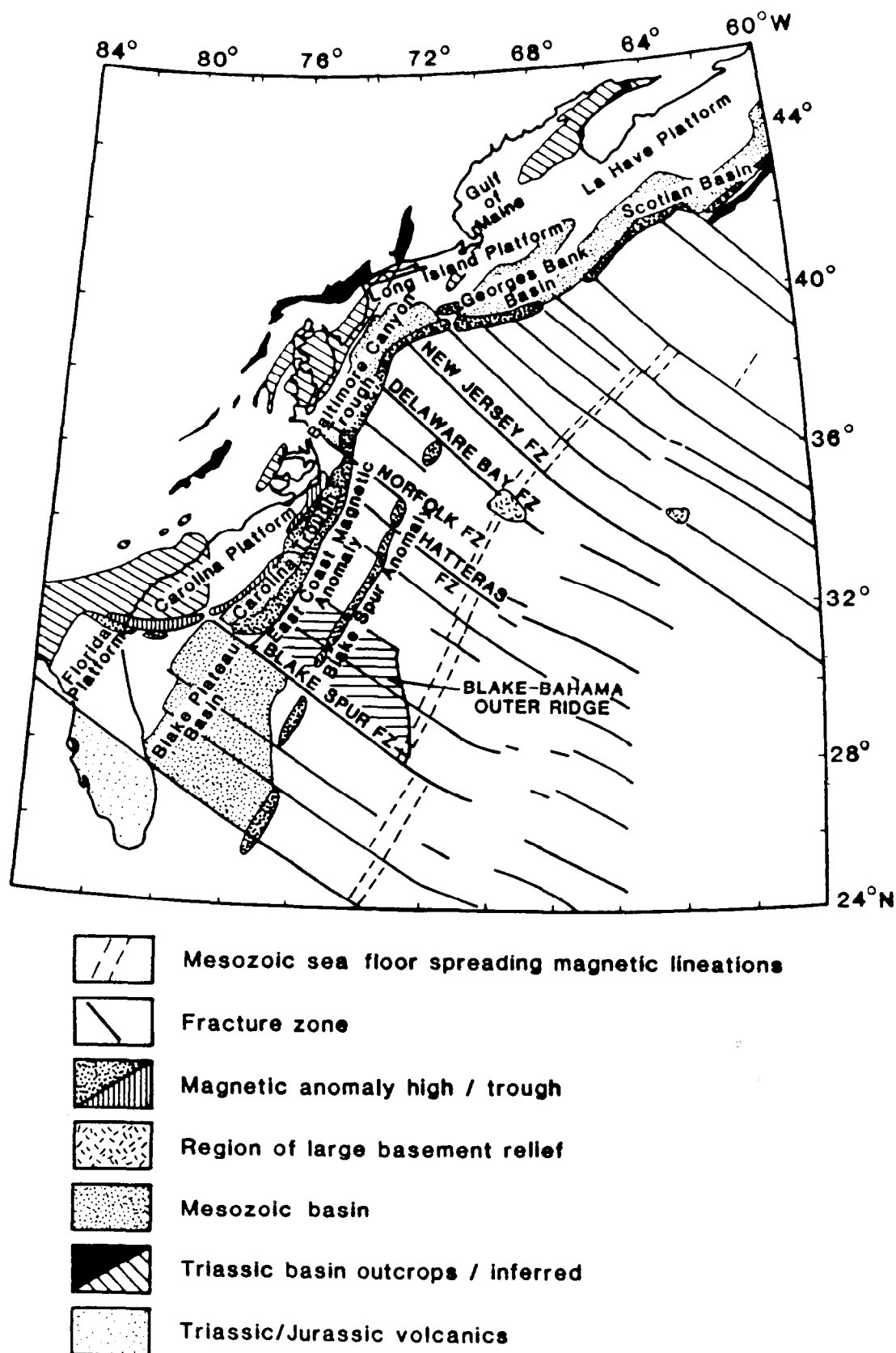
Figure 1. TECTONIC FEATURES OF THE EASTERN CONTINENTAL MARGIN OF NORTH AMERICA

After Grow (1981)

margin to the east and southeast, and weakly magnetized transitional and continental crust beneath the margin to the west and northwest. Such an interpretation is also consistent with the similar location of a positive isostatic gravity anomaly resulting from a drastically thinned continental crust (Hutchinson et al., 1983).

North of Cape Fear the margin above 2,000 m bathymetric depth is less than 150 km wide, whereas between Cape Fear and the Florida-Bahama region the margin broadens to almost 500 km. Beneath this broader region are located the Carolina Trough and the Blake Plateau Basin, both containing greater than 10,000 m of post-rift marine sediments. The marginal broadening is also a result of the oceanward progradation and upward growth of the Blake - Bahama Outer Ridge.

The lateral extent of the individual basins is partly controlled by major fracture zones running approximately perpendicular to the continental margin (Figure 1). Presumably, the topographic expressions of these fractures determined the movement and deposition of sediment, providing intervening topographic highs with reduced sedimentation rates.

Although most of the depositional basins lie landward of the ECMA, the Blake Plateau Basin is exceptional in that it is underlain by a very wide zone of transitional crust changing abruptly to normal oceanic crust seaward of the Blake Escarpment. Apparently, attenuation of the continental crust occurred over a wider area than to the north of the Blake Spur. True ocean crust developed only after a new spreading center developed to the east (Dillon et al., 1979; Kent, 1979; Sheridan, 1978; Klitgord and Behrendt, 1979; and Grow, 1981).

As noted above, further broadening of the continental margin was accomplished seaward of the Carolina Trough (Figure 1) by the growth of the Blake - Bahama Outer Ridge, a major topographic feature lying east of the ECMA which is probably floored by true oceanic crust. Part of the ridge lies above the magnetic quiet zone and part across the Blake Spur Anomaly.

Location and Bathymetry

The geographic position of the Blake - Bahama Outer Ridge relative to other major geological features is shown in Figure 1. The ridge is a NW-SE trending topographic high covering an area of approximately 90,000 km^2, which represents a seaward extension of the continental slope and rise.

The geographic limits of the Blake - Bahama Outer Ridge are not formally defined but the approximate limits can be ascertained from Figure 2. The ridge is more correctly two ridges: a large ridge in the north with up to 2,900 m of relief and about 550 km in length and a more subdued ridge to the south of similar length but only 500 m of relief. Markl et al. (1970) term the large structure the Blake Outer Ridge, and the smaller feature the Bahama Outer Ridge. To the south, the Bahama Outer Ridge merges with the Blake - Bahama Basin and is partly bounded by the Blake Spur to the northwest (Figure 2). To the north and northeast, the Bahama Outer Ridge is bounded by the larger Blake Outer Ridge. The Blake Outer Ridge merges eastward and northeastward with the Hatteras abyssal plain and to the west and northwest with the upper continental slope. In this report the "Blake - Bahama Outer Ridge" is used for the entire study region. The references
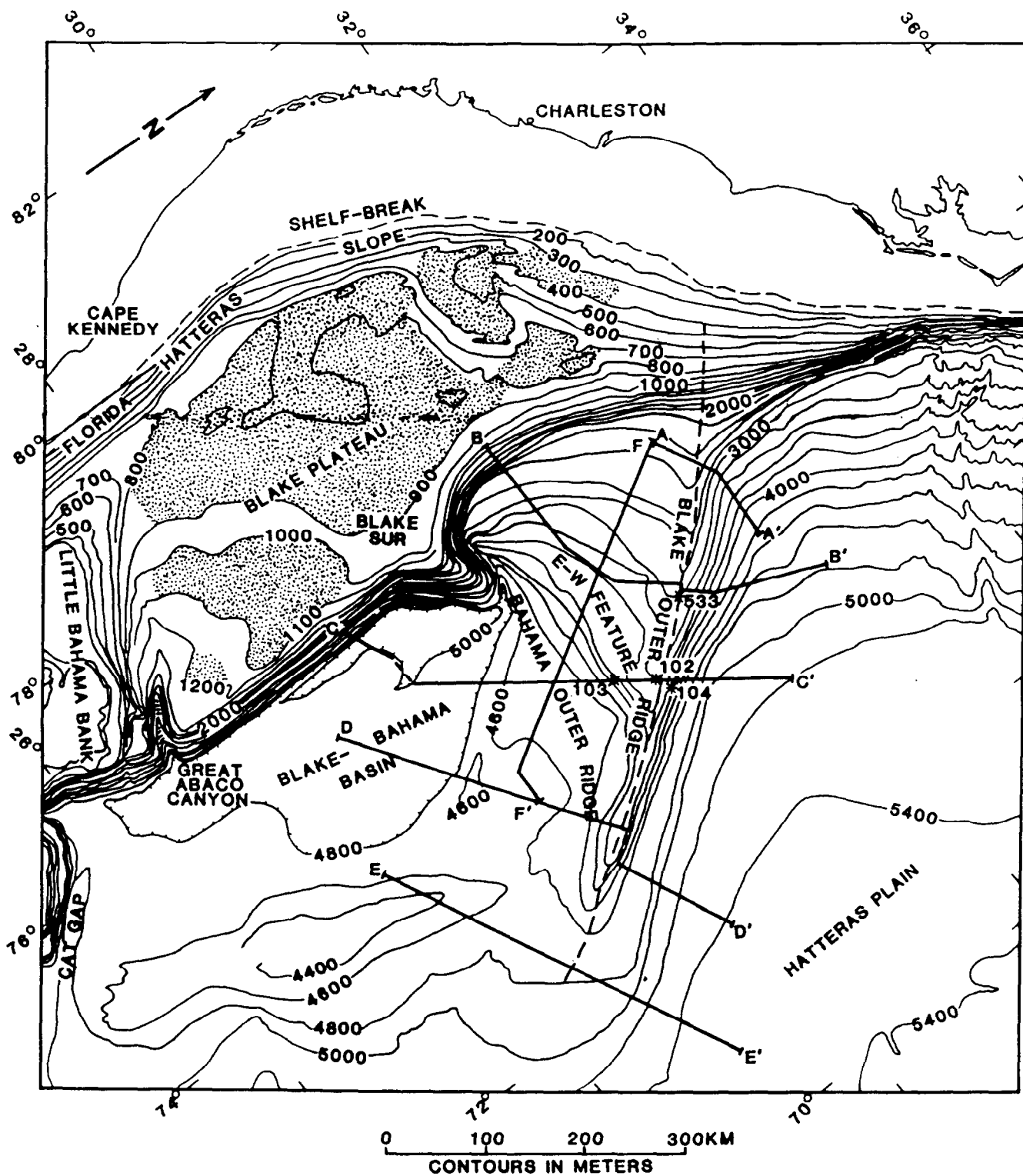
Figure 2. BATHYMETRY OF THE BLAKE-BAHAMA OUTER RIDGE REGION

Based on maps and data in Uchupi (1968),
Markl et al. (1970), Bryan and Heirtzler (1984)

The lines A-A' etc., locate topographic profiles shown in Figures 3A-G. Stippling shows area of active erosion.

"Blake Outer Ridge" or "Bahama Outer Ridge" indicate discussion limited to a specific area.

Figure 2 also locates the topographic cross sections of Figures 3A-G. The topographic data are based upon maps presented by Uchupi (1968), Markl et al. (1970), Bryan and Heirtzler (1984).

Seismic Stratigraphy

The tectonics of the Blake - Bahama Outer Ridge was first studied by Ewing and Ewing (1964) and Pratt and Heezen (1964). Detailed work was performed by Markl et al. (1970) based on LDGO seismic profiles. The most striking surface features are unconformities caused by sediment onlap which help to place the ridges in a relative stratigraphic time frame. An unconformity marks the eastern flank of the Blake Outer Ridge where sediments on the Hatteras abyssal plain onlap the ridge. An unconformity is observed on the northeastern flank of the Bahama Outer Ridge where sediments onlap the western flank of the Blake Outer Ridge (the 30°15' unconformity). The bathymetric expression of unconformities can also be observed to the north of the Blake Spur in the form of a series of NE-SE trending benches.

Markl et al. (1970) recognized two separate ridges, the Blake Outer Ridge to the north, about 550 km long with 2,900 m of maximum relief and the smaller Bahama Outer Ridge to the south of similar length but with only 500 m relief. The sedimentary sequence could be divided into three major acoustic reflectors: horizons A^u (chronostratigraphically representing the A^u unconformity), X, and Y (the bottom simulating reflector of later authors).

Although horizon A^u was originally thought to be a Cretaceous age buried abyssal plain, recent work by Vail et al. (1980) indicates a middle Chattian (late Oligocene) age of 29 m.y. on the continental shelf which corresponds to the beginning of the T_C supercycle of Vail et al. (1977). On the continental rise the A^u unconformity is dated at about 34 m.y. (Rupelian age). According to Jansa et al. (1979) sediments above the A^u reflector (disconformity?) in this region belong to the Blake Ridge Formation.

Reflector X is a poor acoustic reflector; indeed wherever reflector Y is strong, X is infrequently observed. Reflector Y was the first identified on seismic sections by Markl et al. (1970) and corresponds to the bottom simulating reflector discussed by Tucholke et al. (1977), Paull and Dillon (1981), and others. Markl et al. (1970) noted the possibility of reflector Y being a diagenetic boundary rather than a chronostratigraphic boundary.

The A^u unconformity is a regional feature found throughout the western North Atlantic region. Reflector X appears throughout the Blake - Bahama Outer Ridge region and beneath the normal continental rise area to the north where it is closely approximated by the 7 sec. isobath (~5,100 m). It pinches out against reflector A^u to the west beneath the Blake - Bahama Basin, east beneath the Hatteras abyssal plain and south beneath the Cat Gap region. Shipley et al. (1978) and Sheridan et al. (1983) indicate that reflector X separates lower and middle Miocene age sediments in the western North Atlantic.
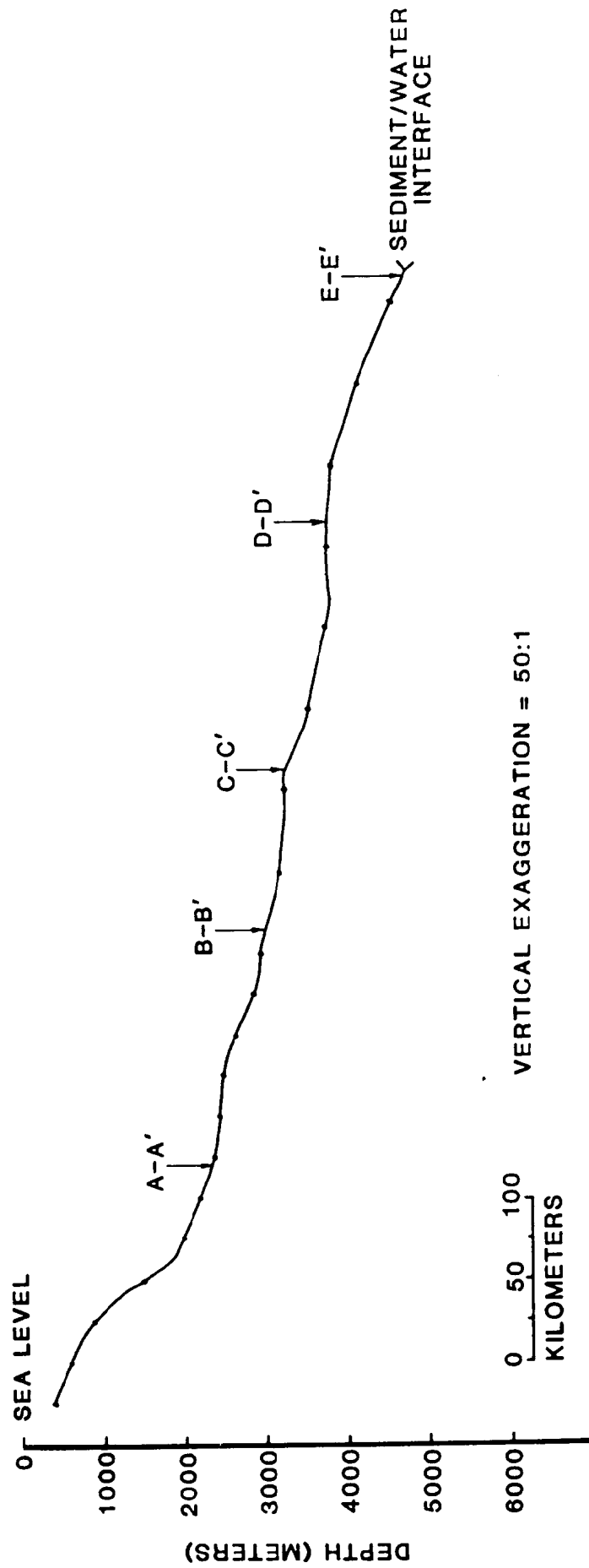
Figure 3A. TOPOGRAPHIC PROFILE ALONG AXIS OF THE BLAKE-BAHAMA OUTER RIDGE REGION

Data referenced in Figure 2.
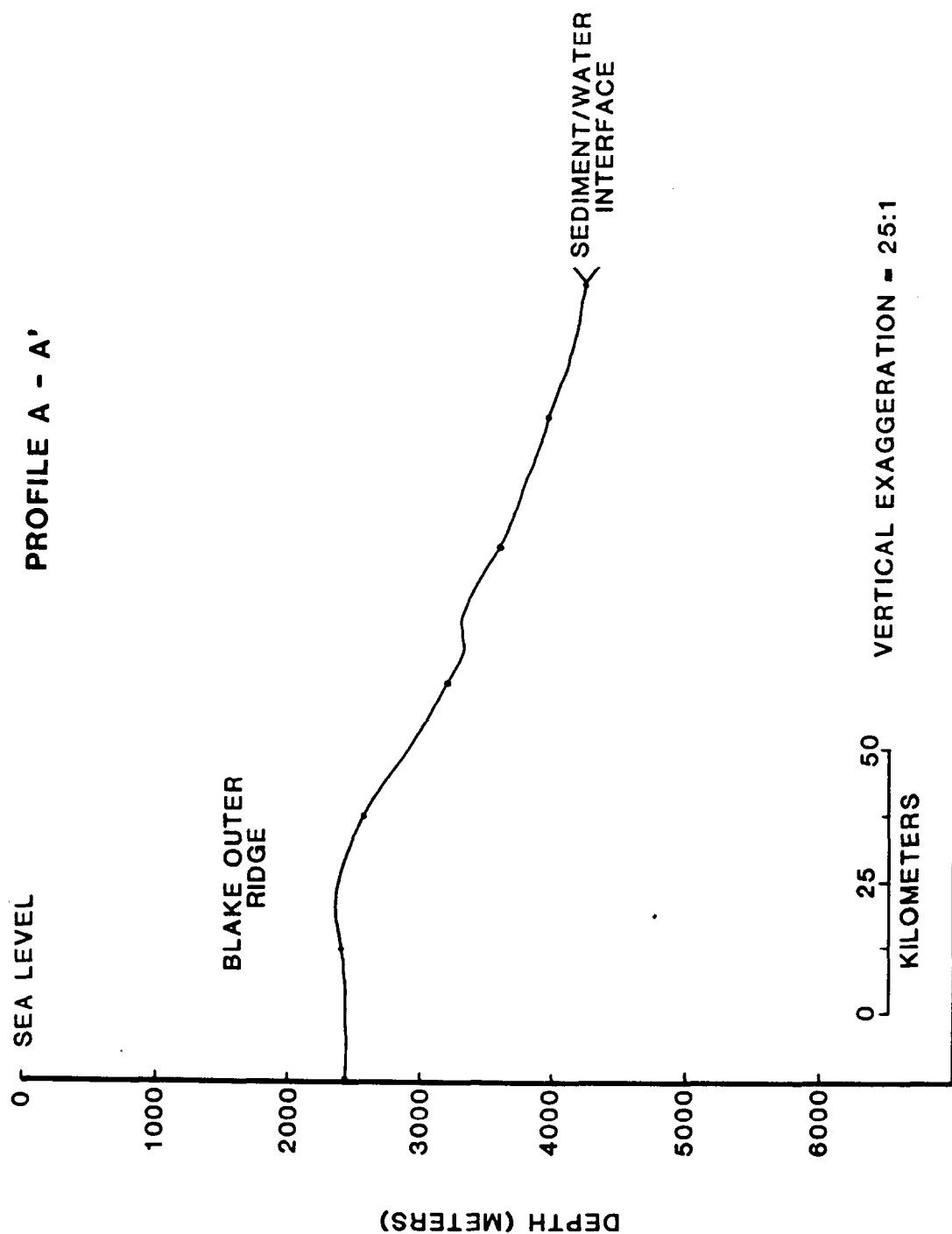
PROFILE A - A'

Figure 3B. TOPOGRAPHIC PROFILE A - A' OF THE BLAKE-BAHAMA OUTER RIDGE REGION

Data referenced in Figure 2.
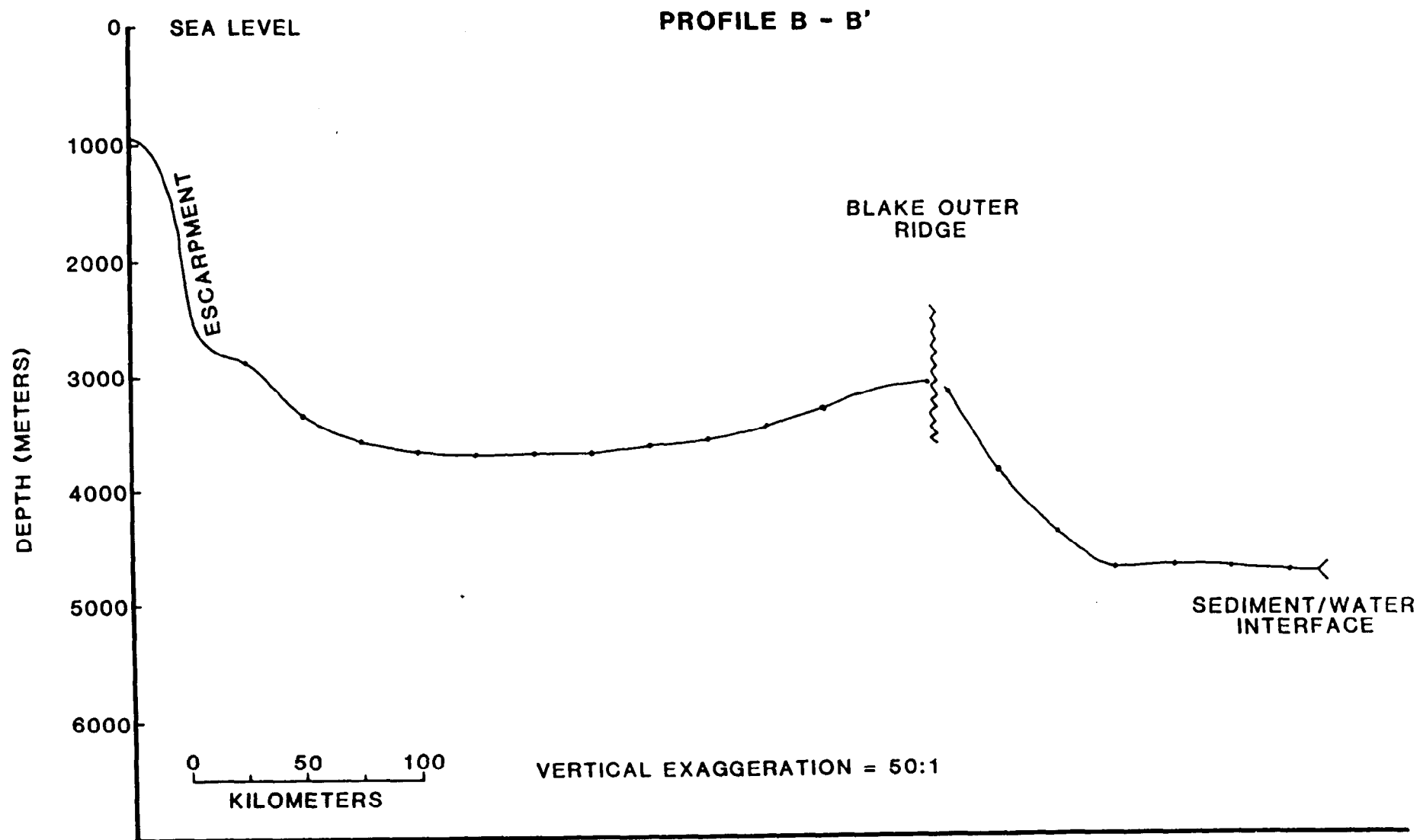
Figure 3C. TOPOGRAPHIC PROFILE B - B' OF THE BLAKE-BAHAMA OUTER RIDGE REGION

Data referenced in Figure 2.
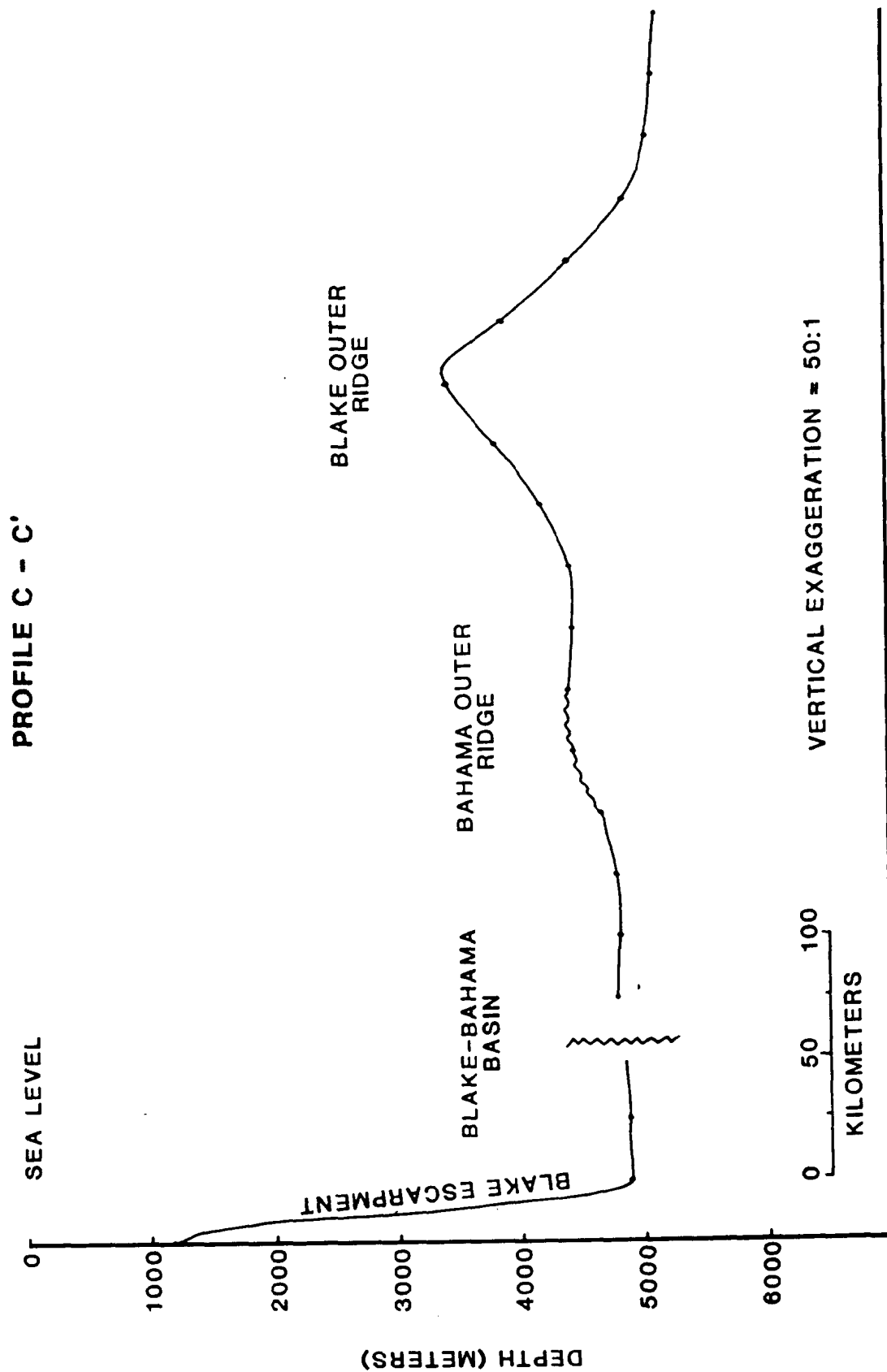
PROFILE C - C'

Figure 3D. TOPOGRAPHIC PROFILE C - C' OF THE BLAKE-BAHAMA OUTER RIDGE REGION

Data referenced in Figure 2.

PROFILE D – D'

SEA LEVEL

BLAKE OUTER
RIDGE

BAHAMA OUTER
RIDGE

BLAKE–BAHAMA
BASIN

DEPTH (METERS)

0
1000
2000
3000
4000
5000
6000

0   50   100

KILOMETERS

VERTICAL EXAGGERATION = 50:1
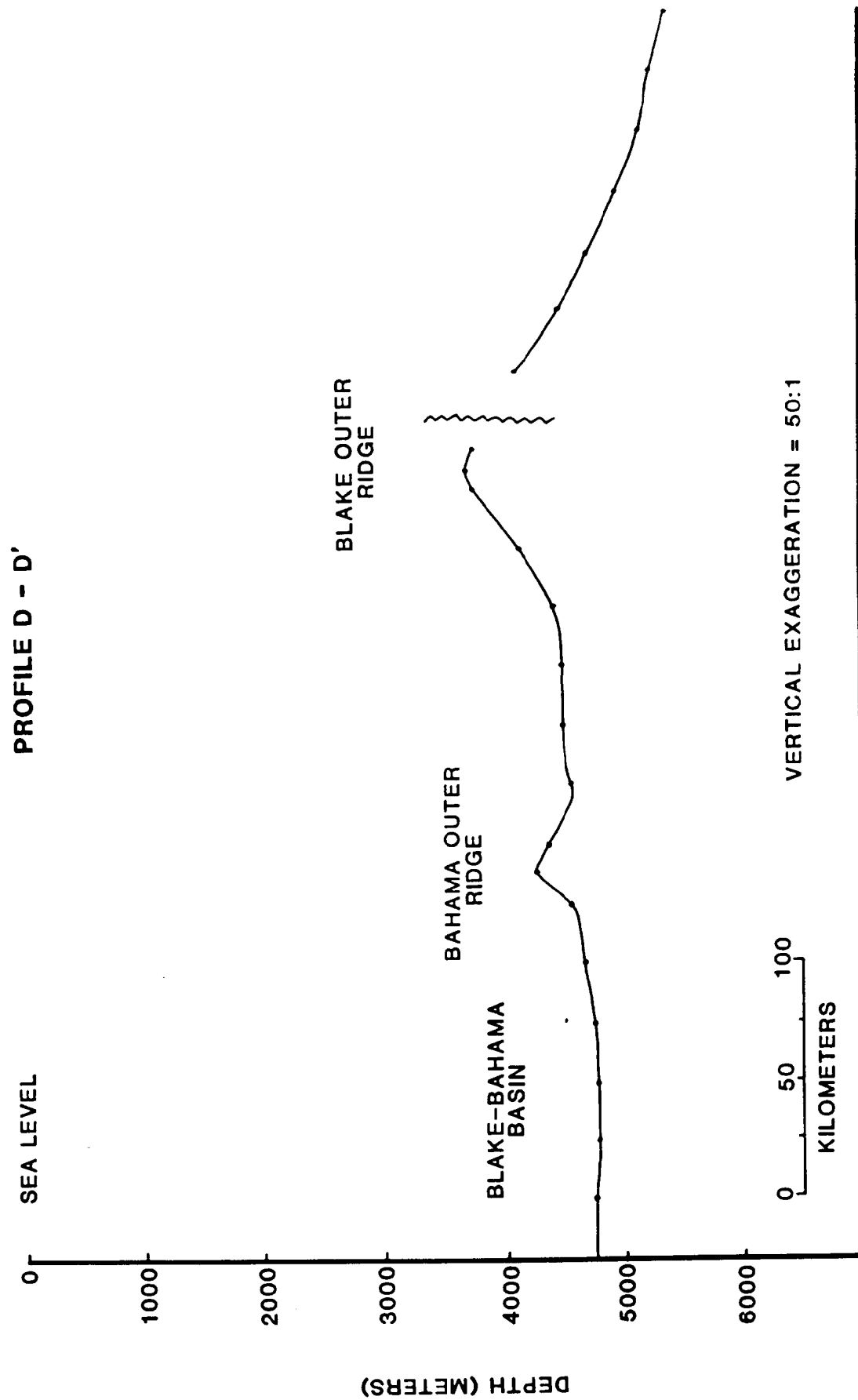
Figure 3E. TOPOGRAPHIC PROFILE D – D' OF THE BLAKE–BAHAMA OUTER RIDGE REGION

Data referenced in Figure 2.

PROFILE E – E'

DEPTH (METERS)

SEA LEVEL

BAHAMA OUTER
RIDGE

BLAKE OUTER
RIDGE

HATTERAS
PLAIN

VERTICAL EXAGGERATION = 50:1

0   50   100

KILOMETERS
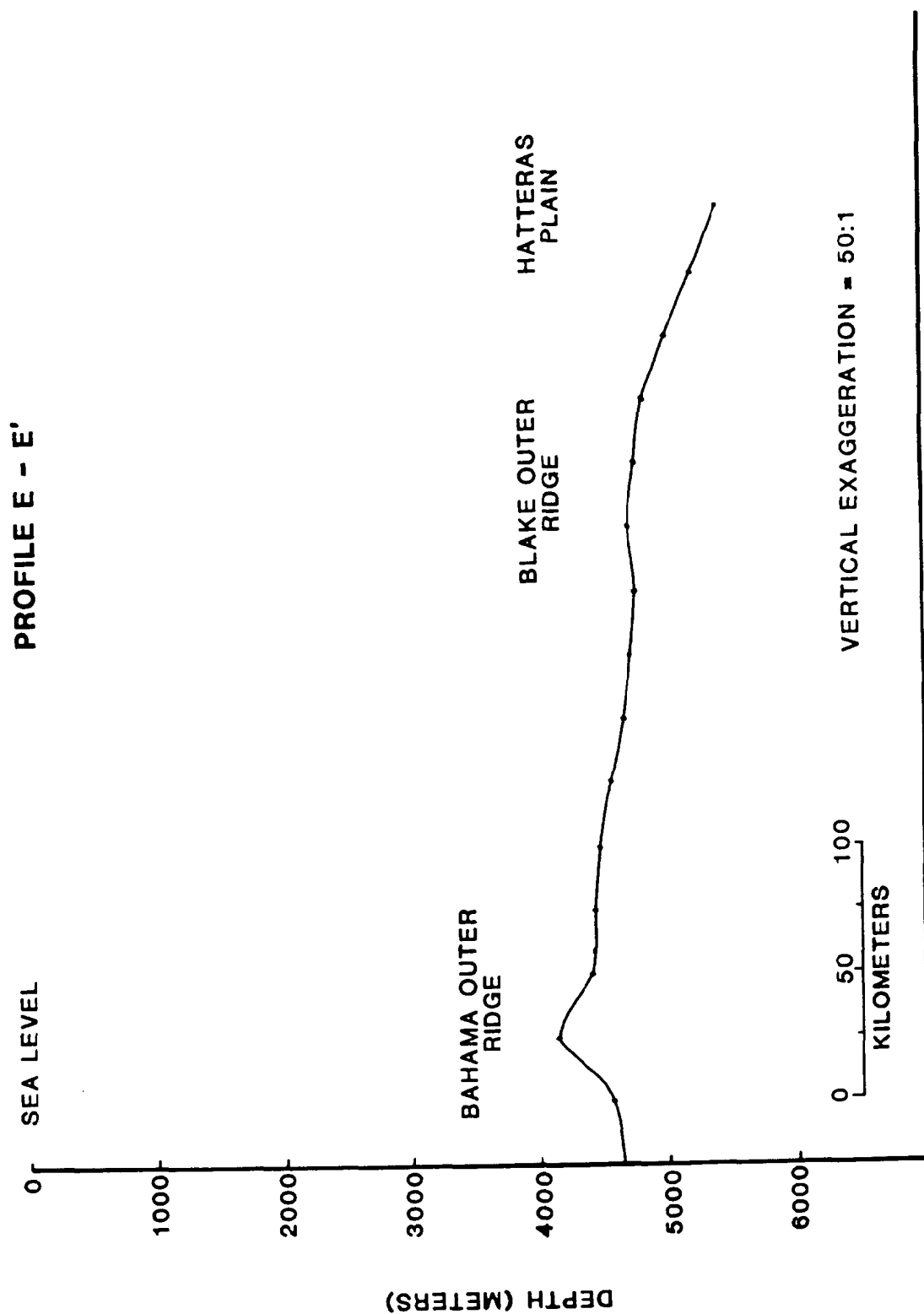
Figure 3F. TOPOGRAPHIC PROFILE E – E' OF THE BLAKE-BAHAMA OUTER RIDGE REGION

Data referenced in Figure 2.
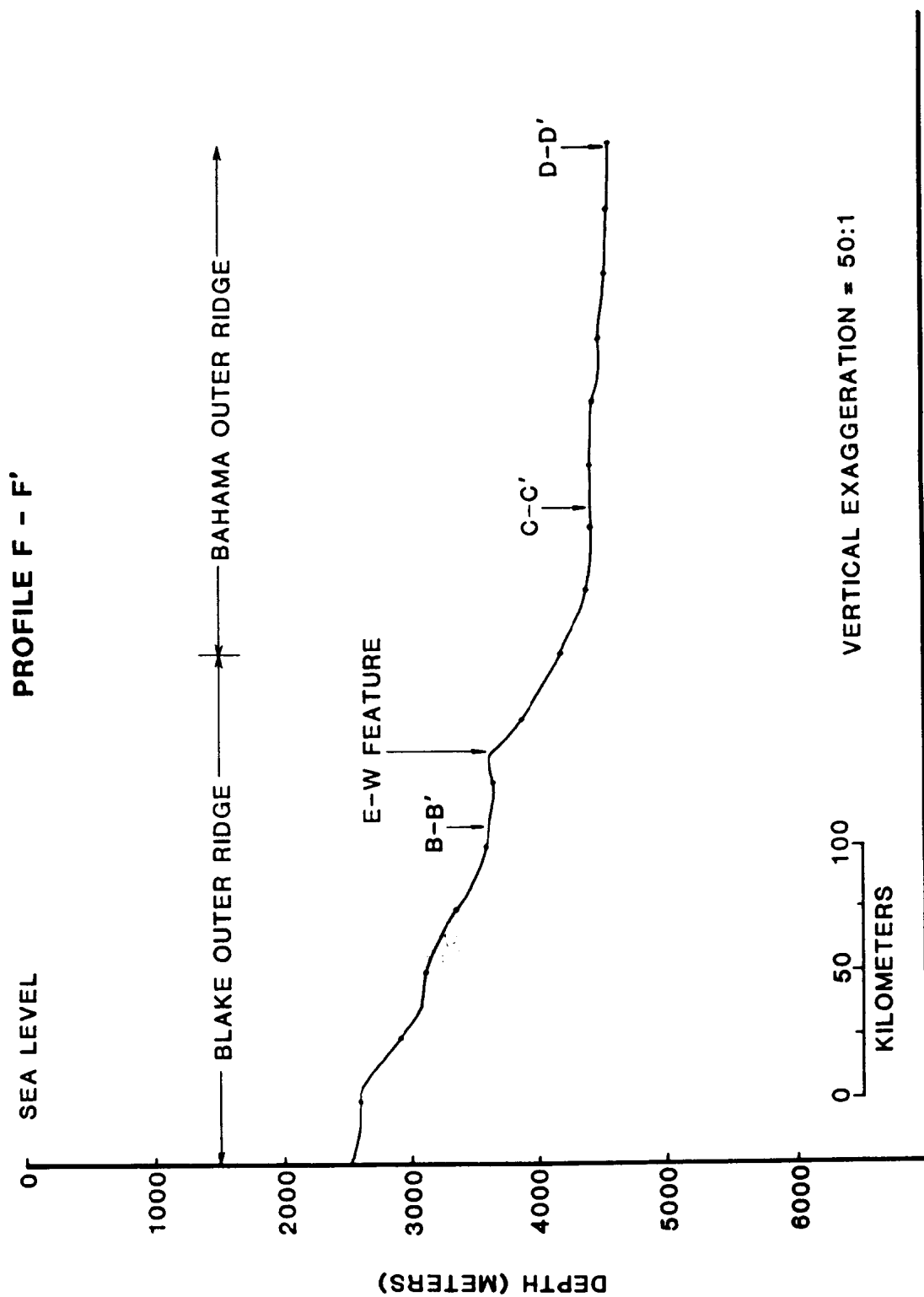
PROFILE F – F'

Figure 3G. TOPOGRAPHIC PROFILE F – F' OF THE BLAKE–BAHAMA OUTER RIDGE REGION

Data referenced in Figure 2.

- 18 -

The acoustic time map to reflector X indicates the overall structure of the region to be about middle Miocene age. The structure of both the Blake and Bahama Outer Ridges was already well established although the crest of the Bahama Outer Ridge was some 33 km east of the present position and the E-W feature had not developed. Sediments deposited during this period are acoustically transparent and have not been sampled during any drilling program.

The post-X structure is somewhat more complicated and the sediments have been divided into a northern regime and southern regime by Markl et al. (1970). The northern regime mantles the Blake Outer Ridge to the north of about 30°30'N. The southern regime is less restricted and extends farther south, roughly through the area bounded by the 6.5 second isobath. Apparently, the two regimes were not deposited contemporaneously, for in places the southern regime onlaps the northern regime. However, in many areas the stratigraphic relations are not clear. Where onlap occurs the southern regime sediments are of Pleistocene to Holocene age and the stratigraphic relations exist because of the nondeposition or erosion of Pleistocene to Holocene sediments on part of the Blake Outer Ridge. By the definition of Markl et al. (1970), the northern regime sediments are divided into two major units by reflector Y, but reflector Y is absent in the southern regime. We now know that reflector Y is a strongly time transgressive boundary without stratigraphic significance. Hence, part of the problem relating the two regimes may be a vagary of their differing acoustic properties rather than a significant stratigraphic complexity. Indeed, Markl et al. (1970) note themselves that the discontinuity sometimes appears to be a facies change between acoustically transparent (northern facies) and stratified (southern facies) material and, hence, results in the difficulty of distinguishing stratigraphic boundaries from acoustic effects. Later work suggests that acoustic dampening is a characteristic of hydrate-bearing sediments.

Geological History

The history of the Blake - Bahama Outer Ridge region has been discussed by Ewing and Ewing (1964), Pratt and Heezen (1964), Heezen et al. (1966), Ewing et al. (1966), Bryan (1970), Markl et al. (1966), and Sheridan et al. (1983).

The Blake - Bahama Outer Ridge can best be described as a positive sedimentation feature developed on the continental slope and rise of the western Atlantic margin. Hence, it should be viewed as a region of focused sedimentation in contrast to the normal pattern of widespread sediment dispersal along the continental margin.

The Blake - Bahama Outer Ridge post-dates the A^u disconformity, hence is younger than 34 m.y. At this time the Blake escarpment was well developed both north and south of the Blake Spur. At the base of the escarpment, the continental rise sloped gently eastward to the Hatteras abyssal plain, as indicated by the subdued nature of the A^u disconformity.

At some undetermined time the current pattern and/or sediment supply changed and deposition was focused along the Blake Outer Ridge. Heezen et

al. (1966) suggested that the Western Boundary Undercurrent played an essential role in determining the sediment distribution through interaction with the northerly flowing turbid Florida current. Hydrodynamic modeling by Bryan (1970) confirmed that such interaction would result in a current flowing roughly southeastward of sufficient magnitude to form the Blake Outer Ridge by sediment deposition. However, the growth of the Bahama Outer Ridge remains unexplained by this model. The age of the outer ridge would be further constrained by the age of the Western Boundary Undercurrent.

Sediment sources for the outer ridge would be from the north, transported south by the Western Boundary Undercurrent, and from the south transported across the Blake Plateau by the Florida current. Paleontological studies of Deep Sea Drilling Project (DSDP) Leg 76 fauna support a dual source, and active current scouring along the Blake Plateau is well documented (Pratt and Heezen, 1964; Ewing et al., 1966; Bryan and Markl, 1966).

Sheridan et al. (1983) endorse the basic model proposed by Bryan (1970) and emphasize the contouring characteristic of the Western Boundary Undercurrent, as evident from the present flow pattern of the current (Markl et al., 1970). Sheridan et al. (1983) explain the growth of the E-W feature as a submarine spit developed south of the Blake Outer Ridge as the contour current swept westward along the southern boundary of the Blake Outer Ridge. Subsequent infilling eventually caused the two features to coalesce. The origin of the Bahama Outer Ridge remains unexplained. The flow of the Western Boundary Undercurrent, contouring the Bahama Outer Ridge allows for sediment deposition if the present flow pattern can be extrapolated backwards in time. However, the ridge was built upon a gently sloping continental rise lacking the necessary topography to initially deflect the southerly flowing boundary undercurrent in the vicinity of the Bahama Outer Ridge.

Stratigraphic Correlation

Stratigraphic correlation at the Blake - Bahama Outer Ridge region rely on: 1) Stratigraphic interpretation of multichannel seismic sections and 2) Core data from DSDP Leg 11, Sites 102, 103, 104 and DSDP Leg 76, Site 533.

Multichannel seismic data are available from the USGS (Paull and Dillon, 1981; Dillon and Paull, 1983; Grow et al., 1981) and from LDGO (Markl et al., 1970; Shipley et al., 1979; Tucholke et al, 1977; Sheridan et al., 1983). The DSDP data are discussed in detail in the Initial Reports of Deep Sea Drilling Project (Boyce, 1972; Hollister et al., 1972; Presley and Kaplan, 1972; Sayles et al., 1972; Claypool and Threlkeld, 1983; Galimov and Kvenvolden, 1983; Kvenvolden and Barnard, 1983; Matsumoto, 1983; Sheridan et al., 1983a, 1983b).

The Blake - Bahama Outer Ridge is built upon transitional continental crust in the west and oceanic crust to the east, as approximated by the position of the east coast magnetic anomaly (Figure 1). Stratigraphic relations within the continental basement are poorly resolved. By extrapolation of onshore information, part of the stratigraphy includes pre- or syn-rift Triassic sediments deposited in half grabens developed within the stretching continental crust.

West of the Jurassic paleoshelf edge, which is now beneath more than 2,000 m of water, a thick wedge of Mesozoic sediments exists above the post-rift unconformity and below the A^u unconformity (Figure 4). Eastward the Mesozoic section progressively thins beneath the Blake Outer Ridge, being only about 600 m thick near DSDP Site 533 (this thickness was calculated based on an acoustic velocity of 2 km/sec for the Mesozoic section (Paull and Dillon, 1981, from a seismic section in Sheridan et al., 1983).

Above the A^u unconformity, Tertiary to Quaternary sediments are thin west of the Jurassic paleoshelf (Figure 4) and form a thick sedimentary wedge in the Blake - Bahama Outer Ridge region. A seismic section near Site 533 and a stratigraphic interpretation are shown in Figure 5, suggesting over 3,000 m of post-A^u deposition in this region involving Oligocene - Holocene sediments. The thickness and distribution of Pleistocene - Holocene sediments are highly variable due to either erosion or non-deposition. In general, Pleistocene to Holocene sediments are very thin or absent on the east flank of the Blake Outer Ridge and are thickest over the Bahama Outer Ridge. Consequently, upper Miocene and Pliocene sediments are observed at the surface or encountered at shallow depth beneath the eastern flank of the Blake Outer Ridge.

The upper part of the Paleocene to Holocene section has been sampled by DSDP Leg 11 and Leg 76 at four sites as follows:

DSDP Leg 11

Site 102. 620 m upper Miocene to Holocene sediments.

Site 103. 450 m upper Miocene to Holocene sediments.

Site 104. 617 m middle-upper Miocene and Pleistocene to Holocene sediments

DSDP Leg 76

Site 533. 400 m of middle Pliocene to Holocene sediments

Lithology

This information is derived from DSDP core data and is therefore of limited application to the Blake - Bahama Outer Ridge region as a whole.

Lithologically, the Holocene to middle Miocene section is very uniform as shown below and in Figures 6A-C:

Site 102. 620 m of easily penetrated gray, dark gray and olive-gray muds. A significant lithologic change appears at about 620 m based on drilling characteristics; the sediments are firmer and drier.

- 21 -

FIGURE 4. Seismic Stratigraphic Interpretation of
U.S.G.S. Line 32, is located in the pocket at the end
of the report.
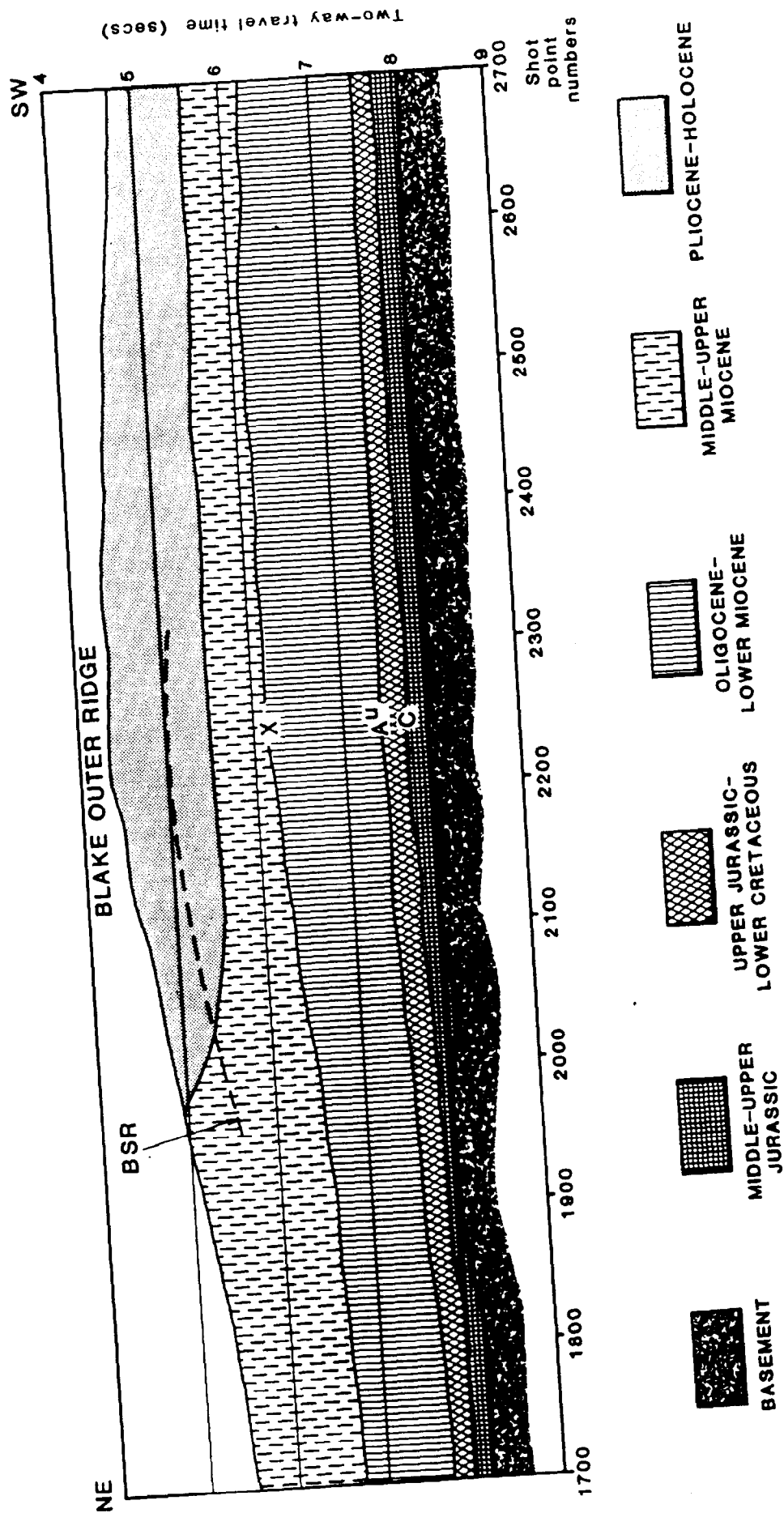
Figure 5. SEISMIC STRATIGRAPHIC INTERPRETATION ACROSS BLAKE OUTER RIDGE

From DSDP Leg 76 Initial Report

PLIOCENE–HOLOCENE

MIDDLE–UPPER MIOCENE

OLIGOCENE–LOWER MIOCENE

UPPER JURASSIC–LOWER CRETACEOUS

MIDDLE–UPPER JURASSIC

BASEMENT
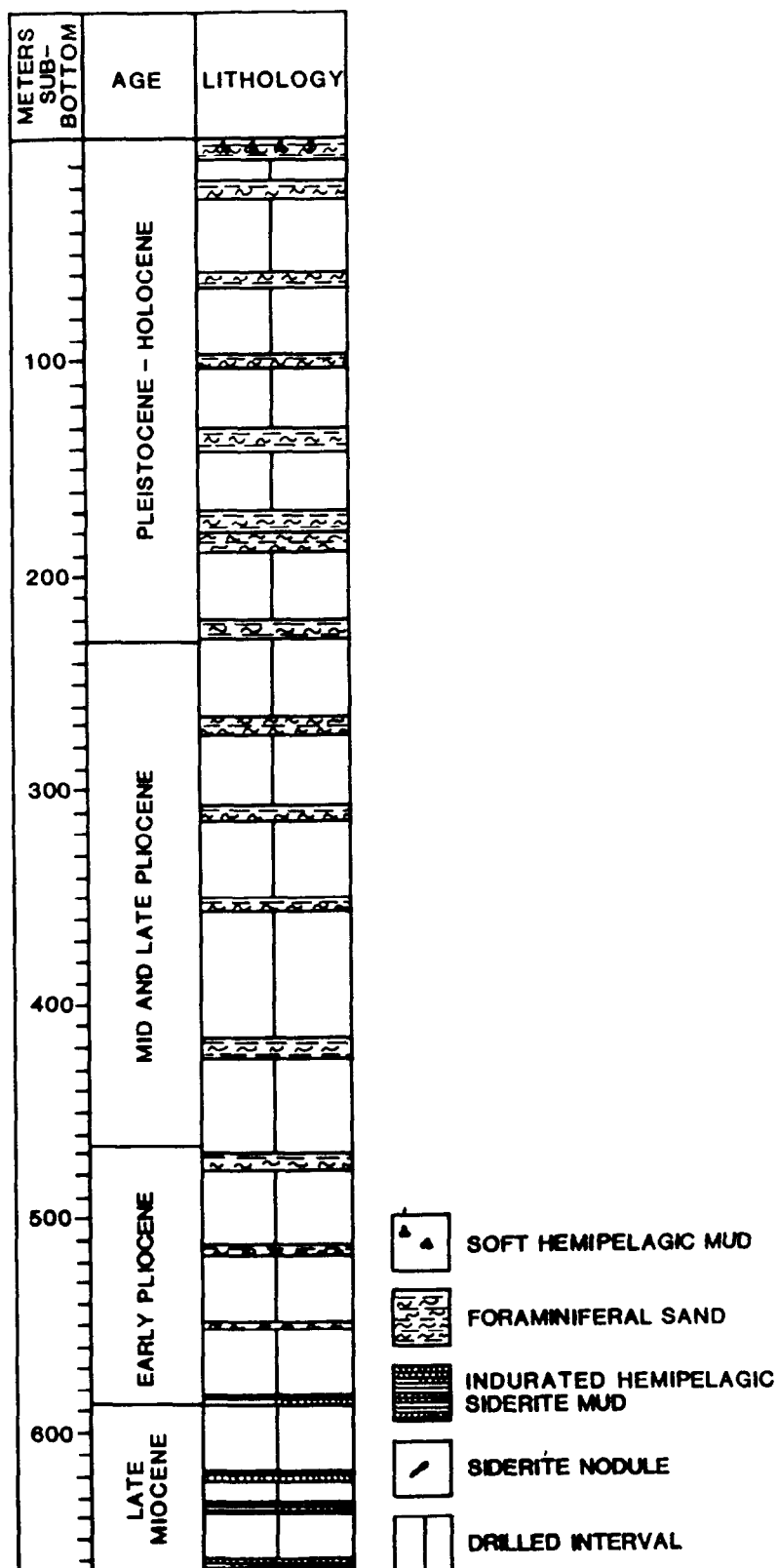
**Figure 6A. LITHOSTRATIGRAPHIC COLUMN FOR DSDP SITE 102
BLAKE OUTER RIDGE**

From DSDP Leg 11 Initial Report

METERS SUB-BOTTOM — **AGE** — **LITHOLOGY**

AGE (Site 104): HOLO-PLEIST, LATE MIOCENE, MIDDLE MIOCENE

Legend (Site 104):

FORAM SAND AND CALCITE CRUSTS

HEMIPELAGIC MUD

DOLOMITE

DRILLED INTERVAL

DSDP LEG 11, SITE 104

AGE (Site 103): HOLO-PLEIST, PLIOCENE, LATE MIOCENE, MID MIOCENE

CORE NUMBER: 1, 2, 3, 4, 5, 6, 7

Legend (Site 103):

FORAMINIFERA SAND

SOFT HEMIPELAGIC MUD

DOLOMITE

INDURATED HEMIPELAGIC SIDERITE MUD

DRILLED INTERVAL
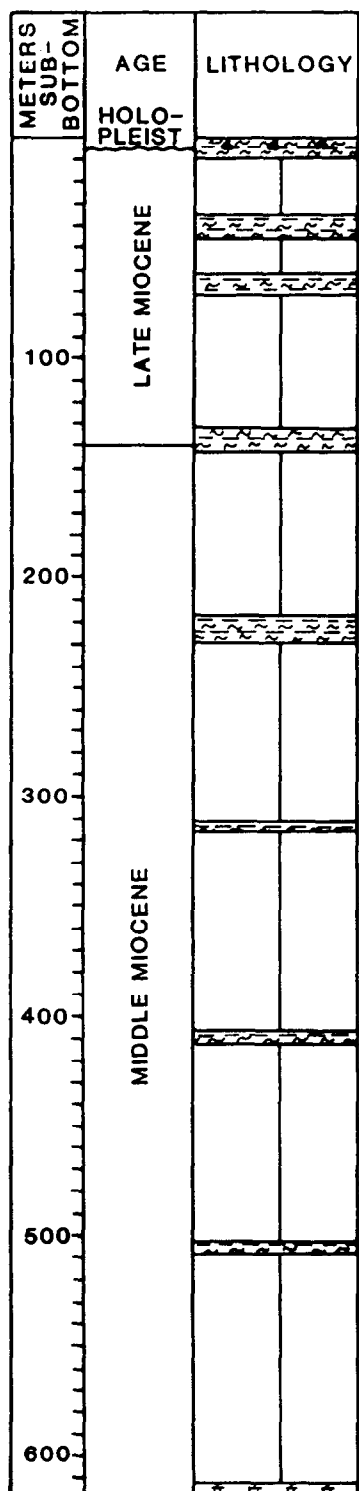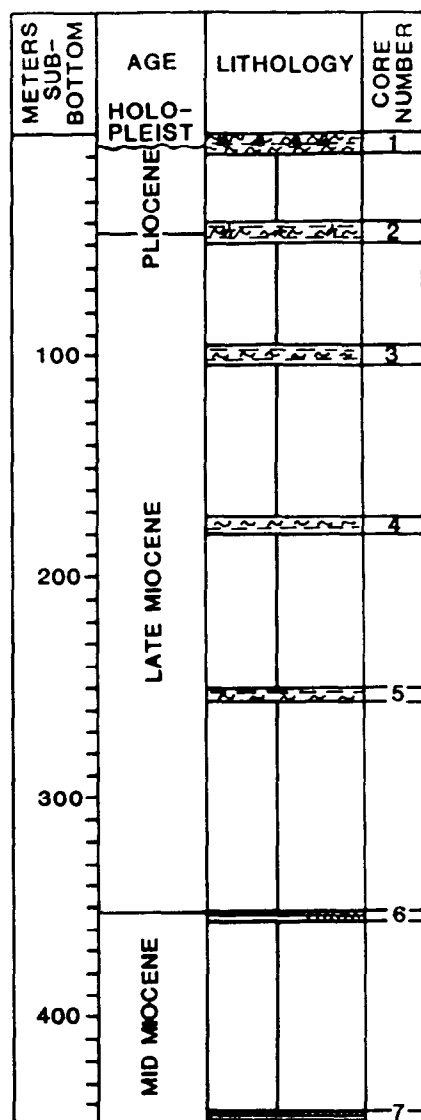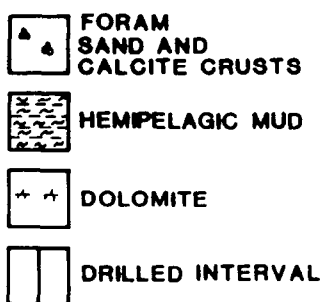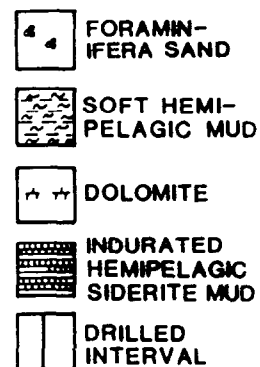
DSDP LEG 11, SITE 103

Figure 6B. LITHOSTRATIGRAPHIC COLUMNS FOR DSDP SITES 103 AND 104 BLAKE OUTER RIDGE

From DSDP Leg 11 Initial Report
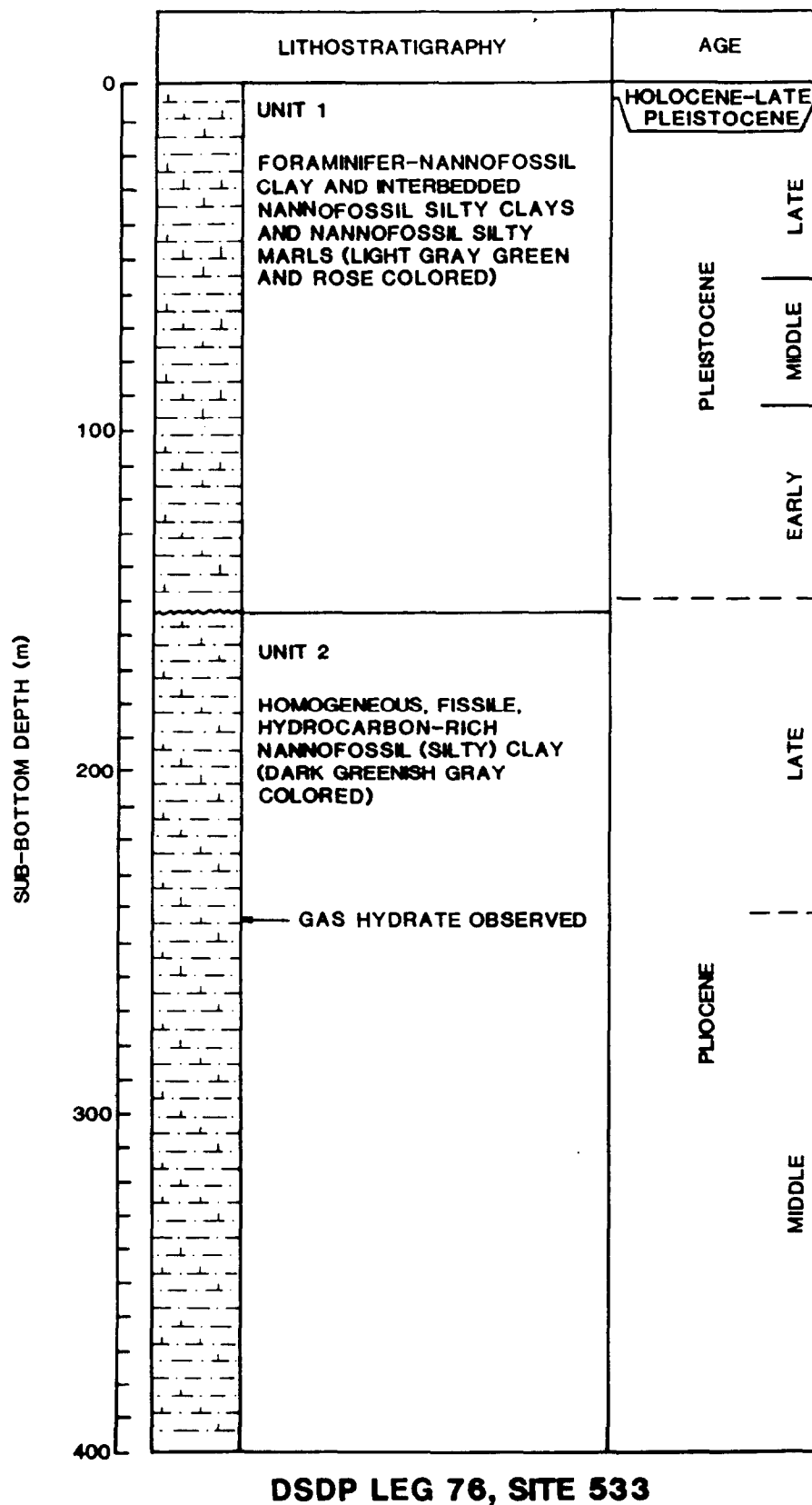
Figure 6C. LITHOSTRATIGRAPHIC COLUMN FOR DSDP SITE 533
BLAKE OUTER RIDGE

From DSDP Leg 76 Initial Report

Site 103. Hemipelagic, silty clays and muds of almost identical character to Site 102.

Site 104. Hemipelagic muds and clays. Drilled through 15 cm of hard ankerite of undetermined lateral extent (may be either a layer or a discrete nodule) at 617 m.

Site 533. Pleistocene and younger sediments are interbedded, moderately burrowed nannofossil marl and hemipelagic silty clays. Layers of dolomite and barite observed at 136 - 140 m depth in silty sediments, replacing clastic matrix and fossil assemblages. Pliocene sediments are stiff, medium to dark greenish-gray silty clays. Diagenetic effects are apparent from the increasing carbonate content in the matrix with depth and occasional appearance of carbonate nodules (161 - 171, 180 - 190, 285 - 294 m).

The physical properties of these muds may be altered by the presence of gas hydrates as discussed by DOE (1983). The most clearly documented physical change in the Blake - Bahama Outer Ridge region is an increase in sonic velocity (Paull and Dillon, 1981; Sheridan et al., 1983) of 20 - 25% over that normally encountered in poorly consolidated muds.

The most complete set of physical property measurements was made at Site 533 and is compiled in Table 2.

TABLE 2

PHYSICAL PROPERTY DATA, SITE 533

Sample (core section, cm from top of section)	Subbottom depth m	Velocity[b] km/s parallel to bedding	Gamma Ray – Wet Bulk Density[a] g/cm^3		Gravimetric			Vane Shear gm/cm^3	Thermal conductivity m x cal/ cm – C – sec
			Parallel to bedding	Normal to bedding	Bulk density gm/cm^3	Water content %	Porosity %		
Hole 533									
1 – 1,000	1.0	1450							
1 – 1,102	1.0		1.48						
1 – 2,56	2.1							82	
1 – 2,71	2.2	1460							
1 – 2,86	2.4	1460							
2 – 2,112	4.6		1.47						
2 – 2,117	4.6	1460							
2 – 2,120	4.6							60	
6 – 1,128	12.7							103	
6 – 1,130	12.7	1470							
6 – 1,131	12.7		1.62						
6 – 3,20	14.6		1.73						
6 – 3.25	14.6							137	
6 – 3,27	14.7	1480							
6 – 3,34	14.7								3.25
7 – 2,93	18.3		1.81						
7 – 2,97	18.4							160	
7 – 2,99	18.4	1470							
8 – 2,111	23.0		1.68						
13 – 2,112	46.5								
13 – 2,114	46.5		1.78					365	
14 – 2,104	49.6							369	
16 – 2,41	57.0		1.82						
17 – 2,56	61.6							451	
17 – 2,82	61.8		1.75						

TABLE 2 (cont.)

18 - 3,3	67.0	1.69					
18 - 3,10	67.1					451	
19 - 2,117	71.2	1.69					
20 - 2,98	75.5	1.66				458	
20 - 2,103	75.5					554	
21 - 2,91	79.9	1.64				623	
21 - 2,98	80.0					785	
23 - 2,96	84.5	1.64					
24 - 2,106	93.6					670	
24 - 2,108	93.6	1.66					
25 - 2,125	98.3	1.72				820	
25 - 2,133	98.3					658	
27 - 3,80	108.3	1.80					
27 - 3,84	108.3	1.71				739	
28 - 3,81	112.8	1.62					
28 - 3,84	112.8					1132	
30 - 2,65	120.6					947	
30 - 2,70	120.7						
31 - 2,76	124.8						
31 - 2,88	124.9						
32 - 1,115	128.2						3.52
32 - 2,81	129.3	1.71				1282	4.11
32 - 2,90	129.4					1143	
32 - 2,99	129.5					1131	
33 - 2,87	133.9	1.63					
34 - 1,102	137.0					739	
34 - 1,104	137.0	1.78					
35 - 2,100	143.0	1.77					
35 - 2,102	143.0		1.72	33.7	57.9	1317	
36 - 1,57	145.6					1686	
37 - 2,76	148.8					1987	
37 - 2,86	148.9		1.70	36.0	60.2		
38 - 2,90	151.9		1.67				3.26
38 - 3,46	153.0						
38 - 3,71	153.2						
38 - 3,72	153.2						

TABLE 2 (cont.)

Sample	Depth							
38 - 3,115	153.6		1.75				1652	3.13
39 - 2,34	155.8			1.67	35.7	59.5		
39 - 3,68	157.7						1756	
40 - 1,113	159.6						1917	
41 - 2,107	165.6							
Hole 533A								
8 - 2,63	192.1	1.64					635	
8 - 2,57	192.1							
8 - 3,99	194.0						486	
13 - 5,124	245.7	1.66						
15 - 2,67	258.7	1.70						
16 - 5,49	272.5	1.66						
17 - 5,110	282.6	1.64						3.19
18 - 5,45	291.4	1.74						2.62
18 - 5,46	291.5							3.29
18 - 5,51	291.5							
18 - 5,92	291.9							
19 - 2,41	296.4	1.69						
20 - 3,58	307.6	1.77						
21 - 4,104	319.0	1.70						
22 - 4,98	328.5	1.63		1.69	34.5	58.3		
22 - 5,77	330.8	1.80						
23 - 4,71	337.7	1.78		1.72	33.5	57.9		
24 - 6,118	350.7	1.75						
25 - 3,23	354.7	1.75						
26 - 3,118	365.2	1.77						
26 - 4,63	366.1							3.23
26 - 4,110	366.6							3.57
26 - 4,120	366.7							3.99
27 - 2,35	372.4	1.72	1.85?	1.74	33.2	57.8		
28 - 2,57	382.1	1.81						
29 - 4,145	395.7							

TABLE 2 (cont.)

Note: blank spaces indicate no measurements were made

a 2-minute count

b The following velocities were measured by Sonobuoys:

Interval	Sonobuoy 1		Sonobuoy 2		Average of two	
	$T_n(s)$	$V_n(km/s)$	$T_n(s)$	$V_n(km/s)$	$T_n(s)$	$V_n(km/s)$
Seafloor to BSR	4.22 - 4.85	2.47	4.26 - 4.89	2.10	4.24 - 4.87	2.28
BSR to X	4.85 - 6.01	2.22	4.89 - 6.19	1.41	4.87 - 6.10	1.81
X to A^u/β	6.01 - 7.41	4.40	6.19 - 7.42	2.83	6.10 - 7.42	3.61

PART II

OCCURRENCES OF GAS HYDRATES

The Blake - Bahama Outer Ridge was initially studied because of the topographic peculiarity of the region compared to the normal continental rise and slope to the north. During these early investigations, seismic reflection profiles across the Blake Outer Ridge showed a strong acoustic reflector at 600 - 700 m depth, termed reflector Y. Markl et al. (1970) noted the possibility that reflector Y may be a shallow diagenetic boundary, possibly related to carbonate cementation. Stoll et al. (1971) demonstrated that anomalously high sound velocity may be generated in sediments containing gas hydrates and, hence, lead to a marked acoustic impedance contrast at the gas - gas hydrate boundary. Consequently, reflector Y, which closely mimics the bottom topography, may be produced by the presence of in situ gas hydrates. In 1972, DSDP Leg 11 cored sediments at Sites 102, 103, and 104 on the Blake - Bahama Outer Ridge that were unusually methane-rich. Lancelot and Ewing (1972) suggested that the bottom simulating reflector (BSR) was due to the presence of hydrates and diagenetic carbonate on the basis of the observed carbonate zonation at the DSDP sites. Detailed examination of multichannel seismic data from LDGO (Tucholke et al., 1977) and USGS (Paull and Dillon, 1981; Dillon and Paull, 1983) and comparison with methane hydrate stability data reinforced the probability that the BSR was caused by a gas hydrate phase change. Further coring in sediments of the Blake Outer Ridge during DSDP Leg 76 confirmed the gas-rich nature of the sediments and recovered a small, but significant, sample of gas hydrate (Kvenvolden and Barnard, 1983).

In the absence of direct recovery of hydrates, the evidence for the presence of hydrate bearing sediment relies heavily on seismic techniques — through the identification of the BSR — and partly on abnormal properties of recovered cores, e.g. sediment disturbance, frothing, and unusual extrusion from the core barrel. If these indirect methods do indicate the presence of gas hydrates, then the Blake - Bahama Outer Ridge must rank as the most thoroughly documented site of offshore gas hydrates. The question remains why gas hydrates should be stabilized in this region while apparently being absent beneath most of the continental slope and rise of the U.S. Atlantic Continental Margin.

Here we review the direct and indirect evidence for the presence of gas hydrates at the Blake - Bahama Outer Ridge, particularly with regard to its volume distribution which remains poorly understood. We also examine the chemical properties which are critical in stabilizing gas hydrates in the context of the geological environment observed at the Blake - Bahama Outer Ridge.

Bottom Simulating Reflectors

An acoustic reflector at about 0.6 sec. subbottom depth is assumed to be a seismic expression of gas hydrates. This return was initially termed reflector Y by Markl et al. (1970) but is presently known as the bottom simulating reflection or BSR. As the name implies, it mimics the bottom topography on most seismic lines. It is most easily identified on tracks at high angles to the topographic contours where it can be distinguished from the generally weaker bedding plane reflections (Figure 7A-D).

Particularly over the Blake Outer Ridge crest, the BSR is a strong reflector, implying a large impedance contrast at the reflection boundary. A detailed examination of multichannel seismic sections by Tucholke et al. (1977) indicates that three classes of reflectors can be recognized:

Class 1: A continuous bottom simulating reflector. The surface is a sharp, high amplitude return at about 0.6 secs subbottom, fading to a diffuse return within 0.2 secs. Such reflections are commonly observed over the ridge crest.

Class 2: The acoustic character is similar to Class 1 returns, however the reflector is not continuous but broken into short segments separated by nonreflective zones. This class usually occurs on the periphery of Class 1 reflections and deeper within the sedimentary section.

Class 3: This reflector is of lower amplitude than either of the above but is noticeably stronger than local bedding plane returns. It is generally observed to be parallel to bedding and the sea floor and occurs adjacent to Class 1 and 2 reflectors, i.e. on the ridge flanks. The Class 3 reflections appear to correlate with intermittent or diffuse reflections noted by Paull and Dillon (1981) in areas where surface erosion may be recognized.

Sediment Acoustic Properties

The BSR is a strong reflector implying a high impedance coefficient. Part of the velocity contrast may result from the increase in sonic velocity created in hydrate bearing sediments (Stoll et al., 1971). Such increases have been measured in laboratory simulations (Halleck, 1982) whereby ocean floor sediments totally saturated with hydrates displayed velocities up to 2.8 km/sec, about a 55% increase over water saturated sediments. Appropriate sonic velocities for the Blake Outer Ridge sediments are not readily derived. Sonobuoy measurements at DSDP Site 533 (Table 2; Sheridan et al., 1983) indicated velocities approaching 2.3 km/sec averaged over the depth from the sea floor to the BSR, a value some 25% higher than commonly measured in normal shallow sediments. Paull and Dillon (1981) and Dillon and Paull (1983), on the basis of velocity analyses at the Blake Outer Ridge, also concluded

A.

DEPTH (METERS)

1000

500

BLAKE OUTER RIDGE

0   10   20KM

N   S

HOLOCENE
PLEISTOCENE

PLIOCENE

VERTICAL EXAGGERATION = 22:1   HYDRATE BASE

Figure 7A.
SECTION OF BLAKE OUTER RIDGE
SHOWING DEPTH TO GAS HYDRATE BASE AND BEDDING REFLECTORS

Based on seismic section in DSDP Leg 76 Initial Report

Depth to gas hydrates base computed assuming an acoustic velocity of 2.25 km/sec.

B.

Figure 7B. SECTION OF BLAKE OUTER RIDGE SHOWING DEPTH TO HYDRATE BASE
AND BEDDING REFLECTORS

Based on seismic time section to BSR from DSDP Leg 11 Initial Report

Assuming an interval velocity of 2.25km/sec.

Figure 7C.   SECTION OF BLAKE OUTER RIDGE SHOWING DEPTH
TO GAS HYDRATE BASE AND BEDDING REFLECTORS

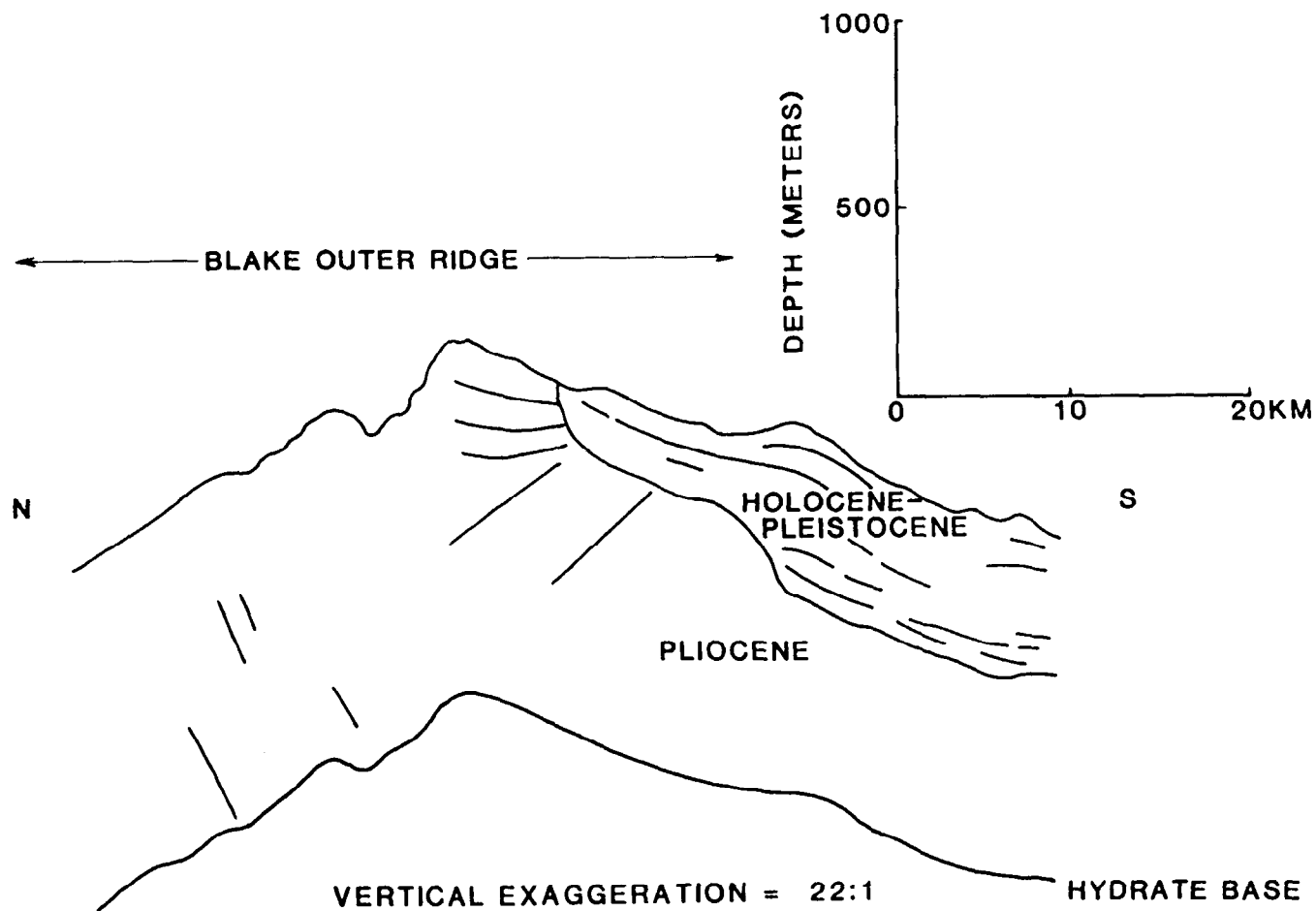Based on seismic time sections shown in Paull and Dillon (1981)
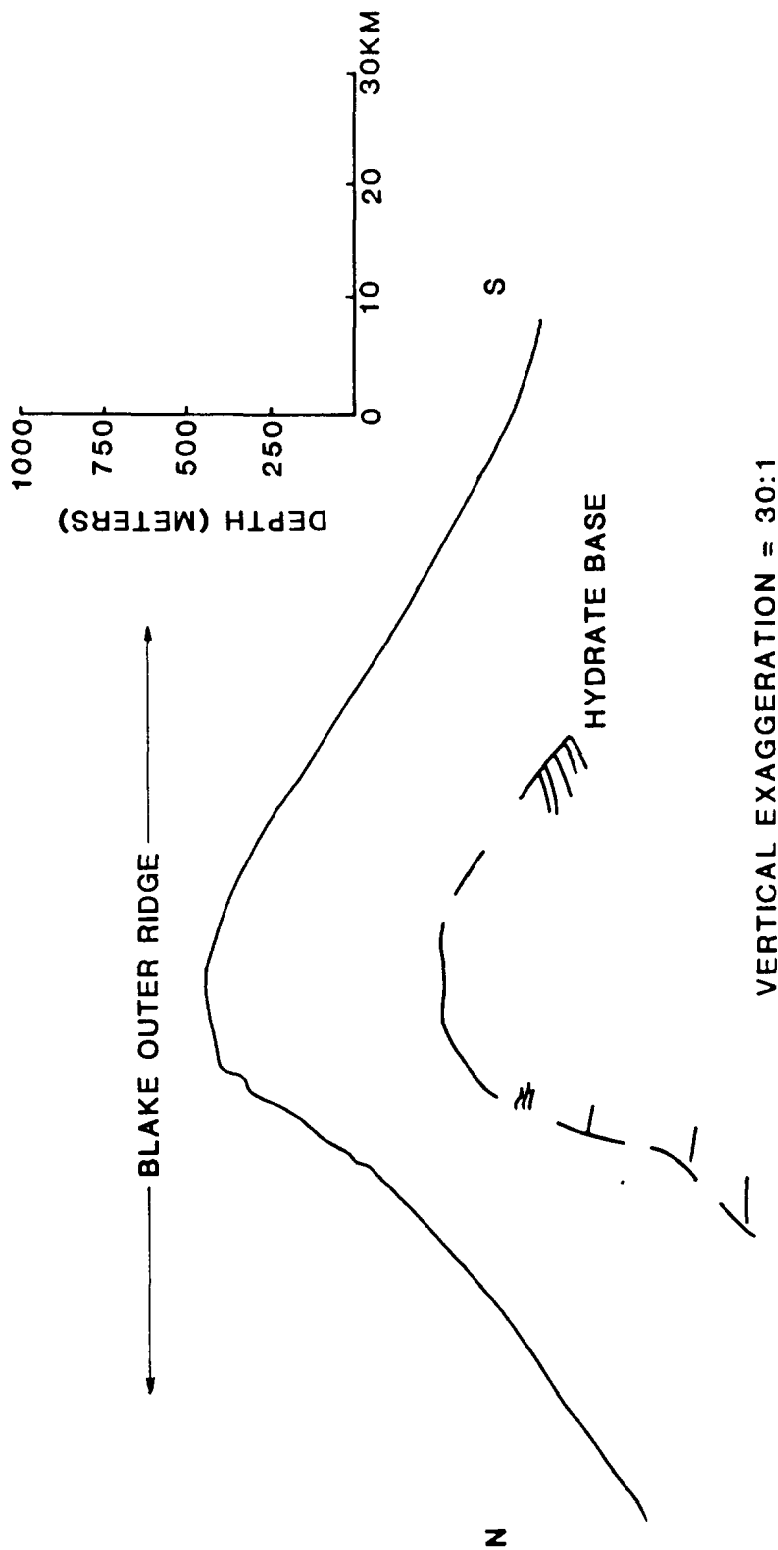
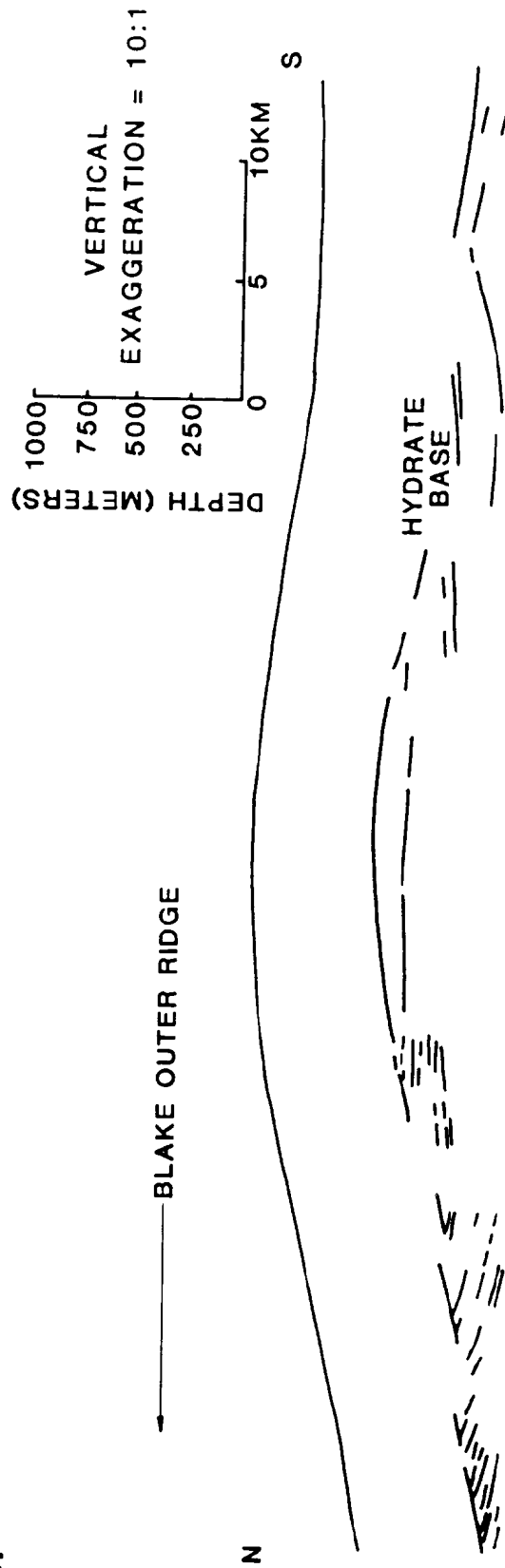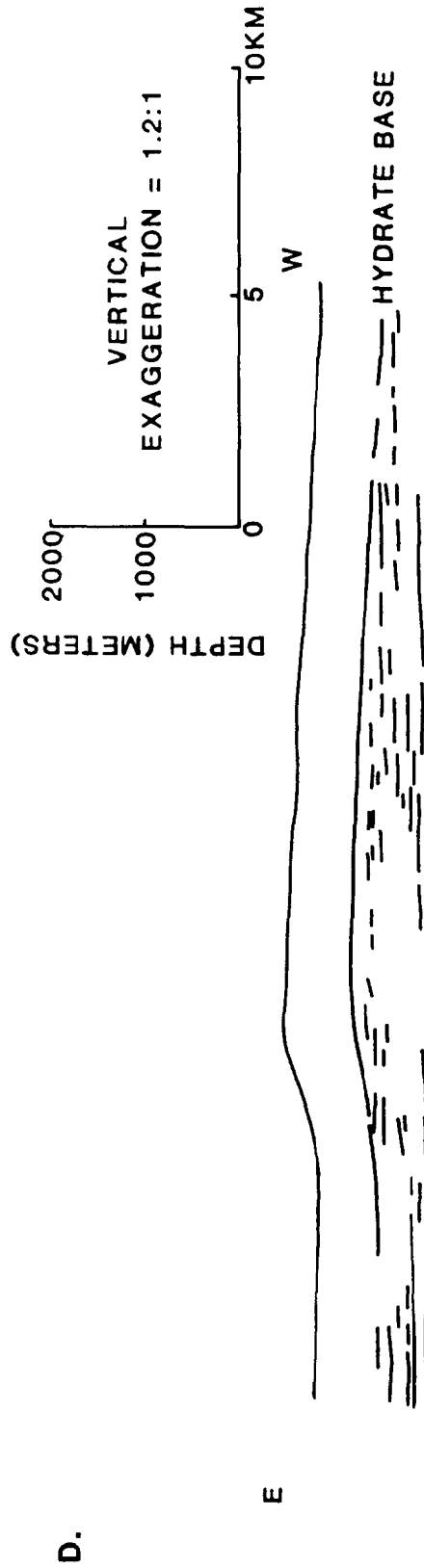Assuming an interval velocity of 2.25km/sec.

Figure 7D. SECTION OF BLAKE OUTER RIDGE SHOWING DEPTH
TO GAS HYDRATE BASE AND BEDDING REFLECTORS

Based on seismic time sections shown in Paull and Dillon (1981)

Assuming an interval velocity of 2.25km/sec.

that the sonic velocities were significantly higher than expected above the BSR (Figure 8). However, the distribution of velocity is somewhat model dependent.

Bryan (1974) has shown that the high amplitude return could not be generated by a hydrate bearing sediment underlain by water saturated horizons because the impedance contrast would be too low. The underlying sediments have to contain an undetermined percentage of gas to lower the interval velocity. The velocity analysis of Paull and Dillon (1981) also demonstrated a velocity inversion at the BSR with a velocity reduction below that of seawater (Figure 8), again implying the presence of a gas zone beneath the BSR. Ultimately the accurate determination of the interval velocity above the BSR becomes a critical measurement, not only in time-depth conversions but also in relating such measurements to laboratory data in order to estimate the amount of hydrates present. To date, there exists an anomaly in that measured velocity values of 2 - 2.2 km/sec (Sheridan et al., 1983) imply hydrate saturation up to 50%, whereas visible examination of recovered core suggests values less than 10%. Several factors may be involved here:

1. The velocities are too variable on a small scale to correlate with core at one site, implying an extremely heterogeneous distribution of hydrate bearing sediment.

2. The sonobuoy measurements are not sufficiently accurate.

3. The sonic velocity may be affected by the geometric arrangement of hydrates in the pore space, e.g. in miniscus regions.

4. The velocity may be determined by both hydrates and carbonate cement.

Distribution of Gas Hydrates

Using multichannel seismic data it is possible to approximately map the distribution of the BSR in the Blake Outer Ridge region (Tucholke et al., 1977; Paull and Dillon, 1981). Such a distribution (Figure 9) presumably also represents the areal extent of the gas hydrate zone. The gas hydrates appear to be concentrated near the ridge crest, the region where Class 1 reflections are most prevalent (Figure 10).

Converting areal extent into an estimate of volume in place is a more tenuous exercise, relying on a knowledge of the vertical distribution of hydrates within the sediment above the BSR. Tucholke et al. (1977) suggest that the gas hydrate layer occupies only the zone directly above the BSR, a distribution which would produce a large impedance contrast but may not explain the overall acoustic opaqueness of the sedimentary section above the BSR. The assumption used to justify such a limited hydrate distribution is that the gas source lies below the BSR, becomes converted to hydrates on ascent into the gas hydrate stability field and consequently blocks further gas migration to shallower levels. This is an arguable scenario because enough gas can be generated by in situ microbial activity (see below) to produce hydrates without necessitating a large component of thermogenic gas.

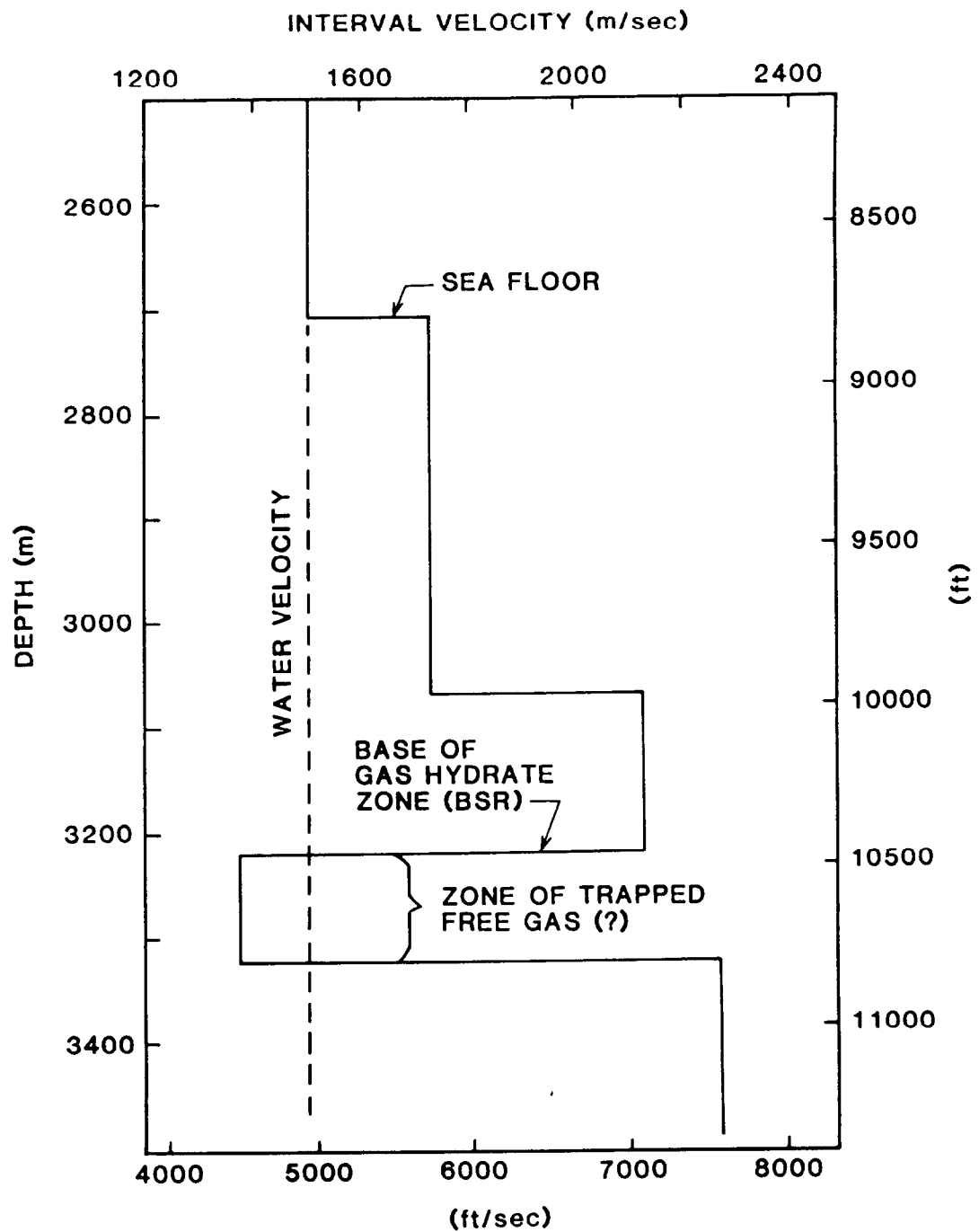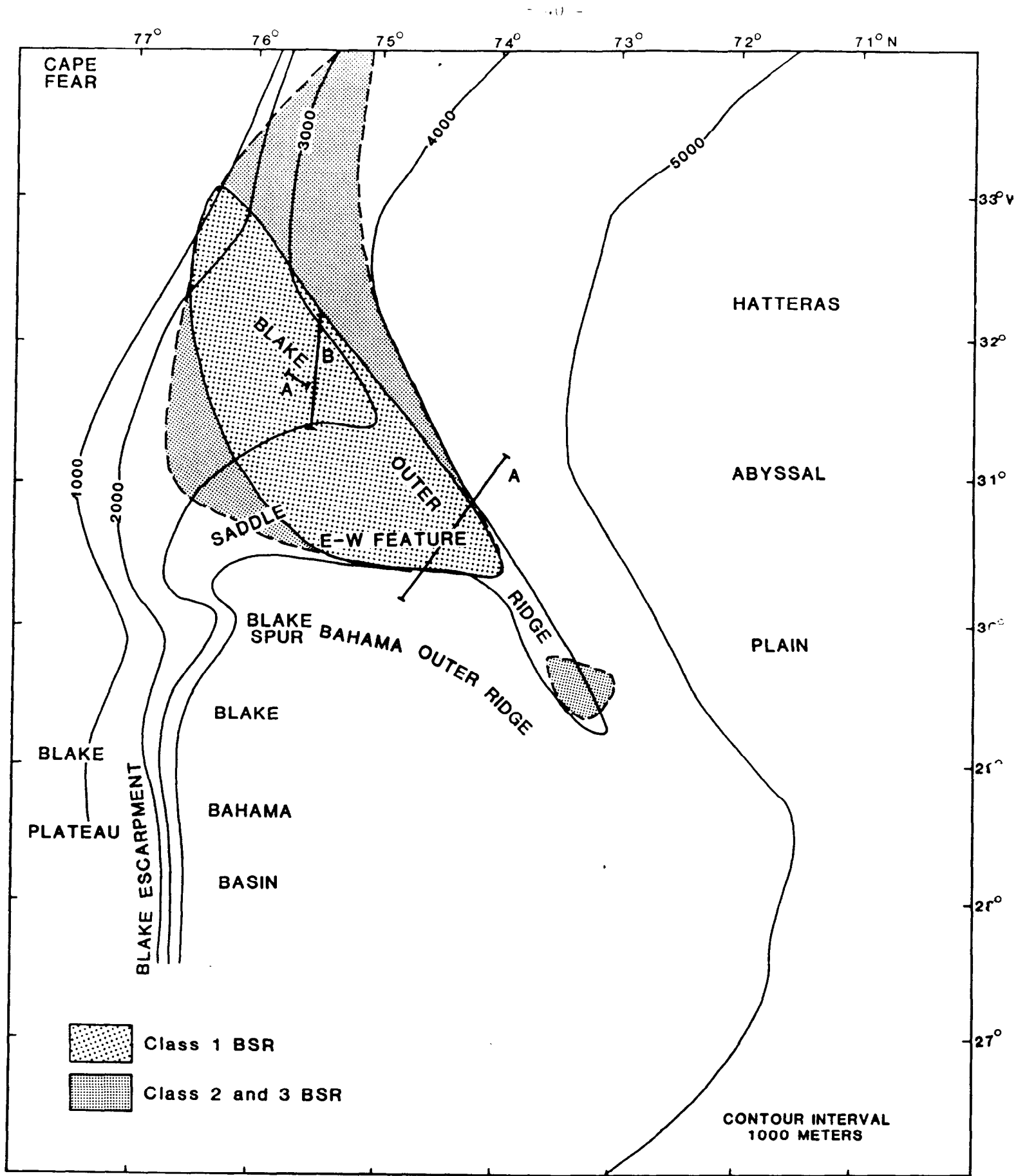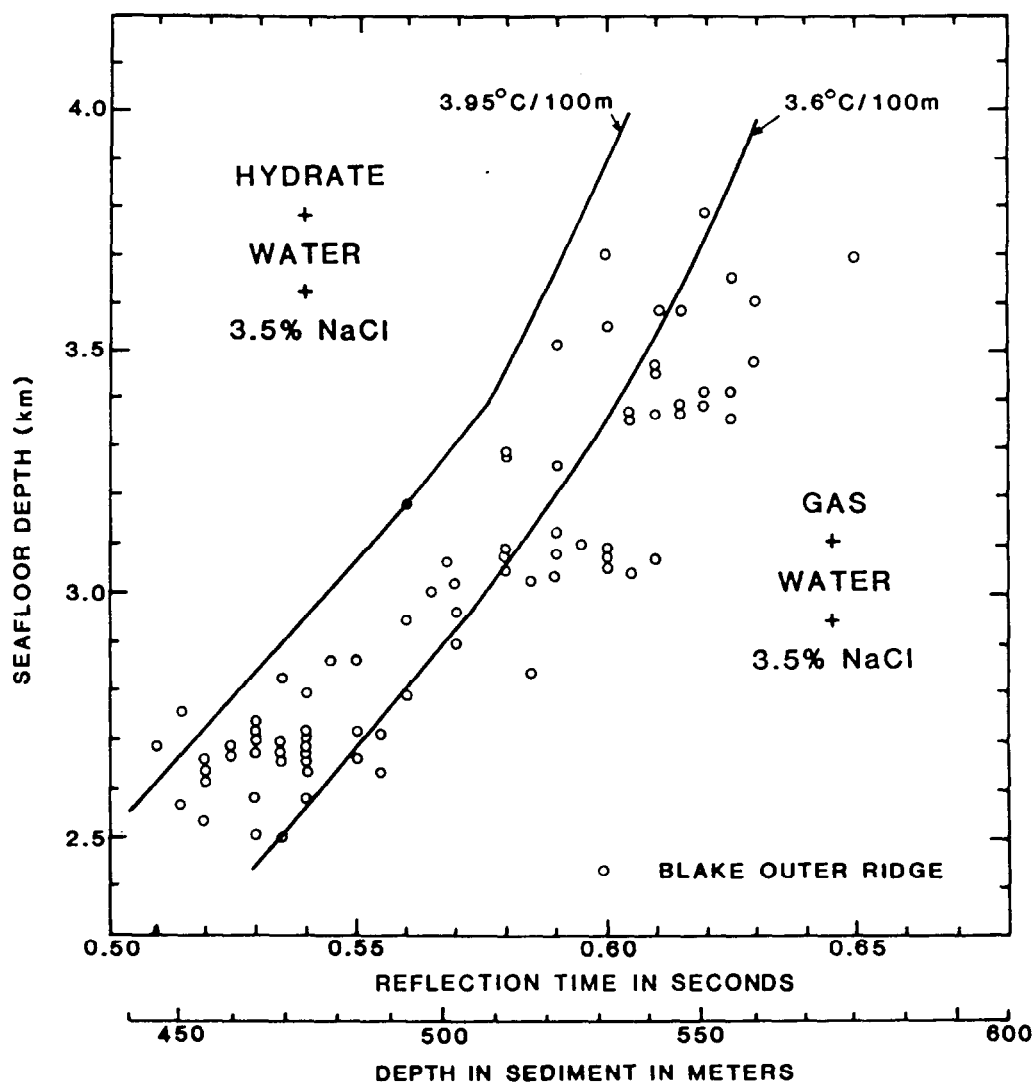**Figure 8. VELOCITY ANALYSIS OF MULTI-CHANNEL SEISMOGRAM ON BLAKE OUTER RIDGE**

After Dillon and Paull (1983)

**Figure 9. AREAL EXTENT OF BOTTOM SIMULATING REFLECTOR (BSR)
IN THE BLAKE-BAHAMA OUTER RIDGE REGION**

Based on seismic data in Paull and Dillon (1981),
Tucholke et al. (1977)

Figure 10. DEPTH TO BOTTOM SIMULATING REFLECTOR AS FUNCTION OF SEA FLOOR DEPTH

Modified after Tucholke et al. (1977)

Hence, the vertical distribution of the hydrate zone cannot be determined on the basis of an underlying thermogenic gas source. It is interesting to note, however, that the velocity profile of Dillon and Paull (1983, Figure 8) also implies a zone of hydrate bearing sediment near the BSR. Indirect evidence from the physical state of sediment cores (Lancelot and Ewing, 1970; Kvenvolden and Barnard, 1983) suggests that hydrates are distributed to some extent well above the BSR.

Presence and Absence of the Bottom Simulating Reflectors

One of the more fascinating aspects of the BSR is the areal change in character, as described above. Such variations require explanation if the BSR is to be used as an indirect indicator of hydrates.

Tucholke et al. (1977) assumed that the presence of the BSR required not only the stabilization of hydrates but also a concentration of gas beneath the hydrate cap. The BSR was thus explained in terms of a gas migration model which attempted to justify not only the observed distribution of the BSR in the region of the Blake - Bahama Outer Ridge but also its absence over almost all other regions of the western Atlantic Continental Margin. In this model, the development of gas-rich sediment beneath the hydrate zone is determined by the geometric relationship of the gas hydrate zone to underlying bedding planes. This relation at the Blake Outer Ridge is optimal for gas accumulation because landward dipping strata restrict the landward migration of gas whereas the hydrate zone, dipping gently seaward, blocks the seaward migration. The absence of gas accumulation beneath the normal continental slope and rise is explained because the sediments here generally dip seaward and gas can migrate and escape landward. The critical aspect of this plausible model lies in the potential for lateral gas migration in shallow dipping clay-mud sediments as opposed to vertical movement due to buoyancy, or even if large-scale gas migration in any direction is possible in essentially nonreservoir lithologies.

Paull and Dillon (1981) have also recognized that the BSR is intermittent to diffuse on the Blake Outer Ridge flanks, particularly beneath areas of major surface erosion to the north. They concluded that depression of the local geotherms as a result of erosion would displace the gas hydrate lower boundary downwards. Under these circumstances, free gas and pore fluid originally beneath the BSR become hydrates and the velocity contrast is lost, therefore the BSR disappears. It should be noted that in lithologically uniform sediments, erosion does not simply depress the geotherms but initially causes an increase in the local geothermal gradient of a magnitude determined by the erosion rate and sediment diffusivity. Table 3 below indicates the magnitude of the gradient changes for different erosion rates.

TABLE 3.

THERMAL GRADIENT CHANGE AS FUNCTION OF EROSION RATE

Erosion Rate mm/yr	Diffusivity cm²/sec	Temperature Gradient* °C/100 m
0	.004	3.87
.3	.004	4.33
.8	.004	5.37
17	.004	6.17

*Assumes a heat flow of 1.0 HFU into sediment column.

The process can best be understood by realizing that the ultimate effect of erosion is to cool the sedimentary column which consequently has to lose heat. This is attained by a local increase in heat flow to the surface with an attendant increase in geothermal gradient. The affect of erosion on gas hydrate stability is illustrated in Figure 11. If the base of gas hydrates is much deeper than the erosional surface and the erosion is too rapid to allow concurrent adjustment of geotherms, then the base of the hydrate zone, i.e. the BSR, will remain undisturbed. Hence, the depth to the base of the BSR will decrease by an amount approximately equivalent to the total erosion. In time the thermal profile equilibrium and the hydrate base gradually moves downward toward a new equilibrium position, i.e. the BSR increases in depth beneath the sea floor.

One potential consequence of this cooling is as follows. If the original base was a zone of hydrate enrichment, then it will remain intact but will now lie well within the zone of hydrate stability. Also, if the underlying gas reservoir was a gas-dominated pore system, then hydrate formation in this zone would be limited and hydrates would exist with free gas. A velocity contrast would be generated between the "stranded" hydrate base and the underlying gas + hydrates, possibly resulting in a strong reflector. The new hydrate base would be developed under the newly established pressure and temperature conditions, and trapping of gas below would give yet another velocity contrast and a strong reflector. Note also that if we assume that pressure conditions within the sediment are hydrostatic then removal of sediment will have no effect on the sediment pore pressure.

Bottom Simulating Reflectors and Salt Diapirism

A number of salt domes penetrate the Blake Outer Ridge near the Carolina Trough. Twenty-three such structures have been located along the axis of the east coast magnetic anomaly, corresponding to the abrupt change in crustal thickness. The source of the diapirs is probably at about 11,000 m subbottom depth and represents early rifting evaporites subsequently mobilized due to sediment overburden.

Paull and Dillon (1981) show seismic sections through two salt dome areas in about 1,500 m of water in which the BSR rises to shallow depths along the flanks of the domes (Figure 12). These perturbations could result
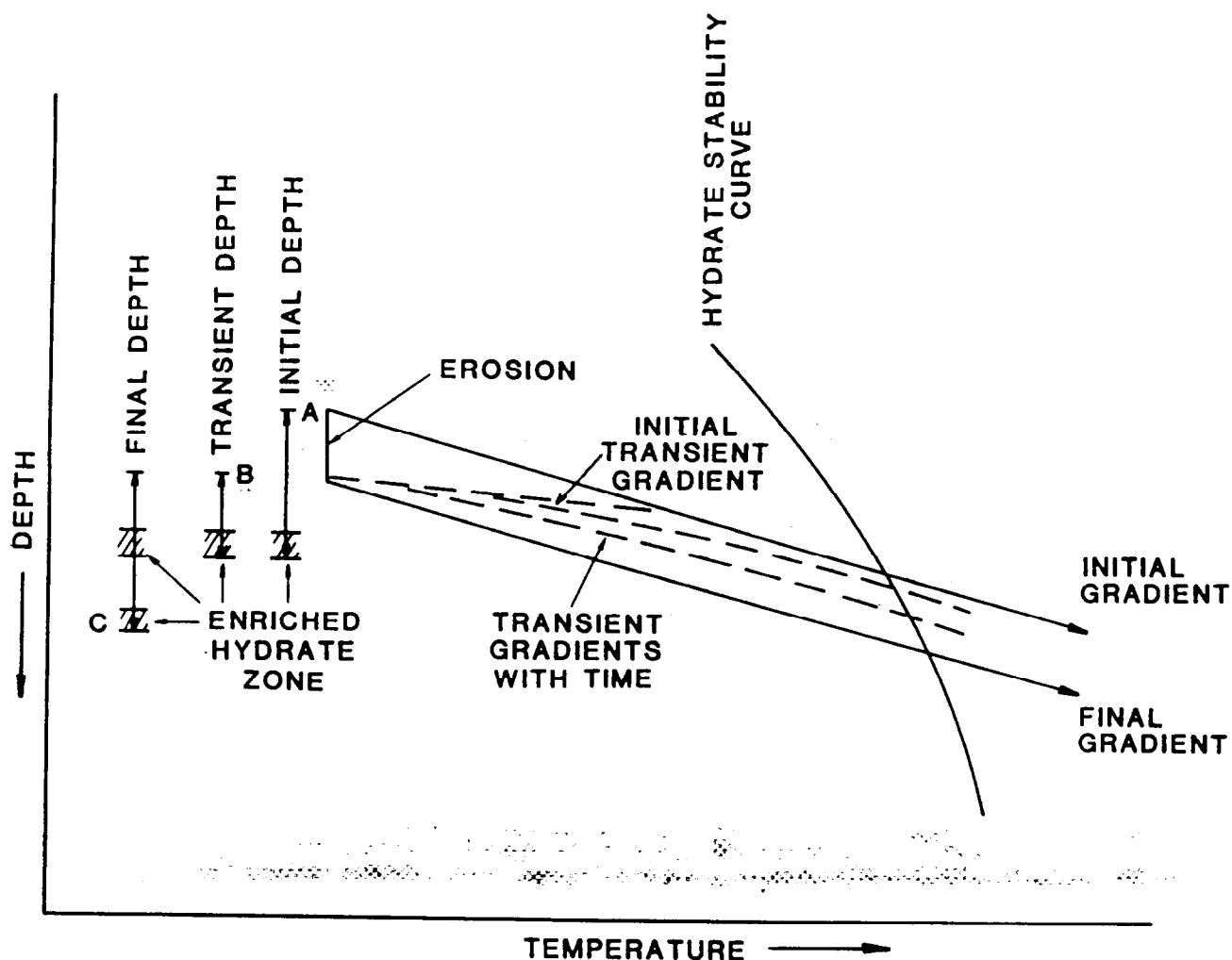
Figure 11. DIAGRAMMATIC REPRESENTATION OF EROSIONAL EFFECTS ON HYDRATE STABILITY

The initial steady state gradient is shown prior to erosion. Following erosion, a near surface transient gradient develops which gradually diminishes to the final steady state gradient. The initial top of the hydrate zone (A) deepens following erosion (B) but the base remains fairly steady. As the final steady state gradient develops, a new base is formed (C) leaving a stranded enriched zone.
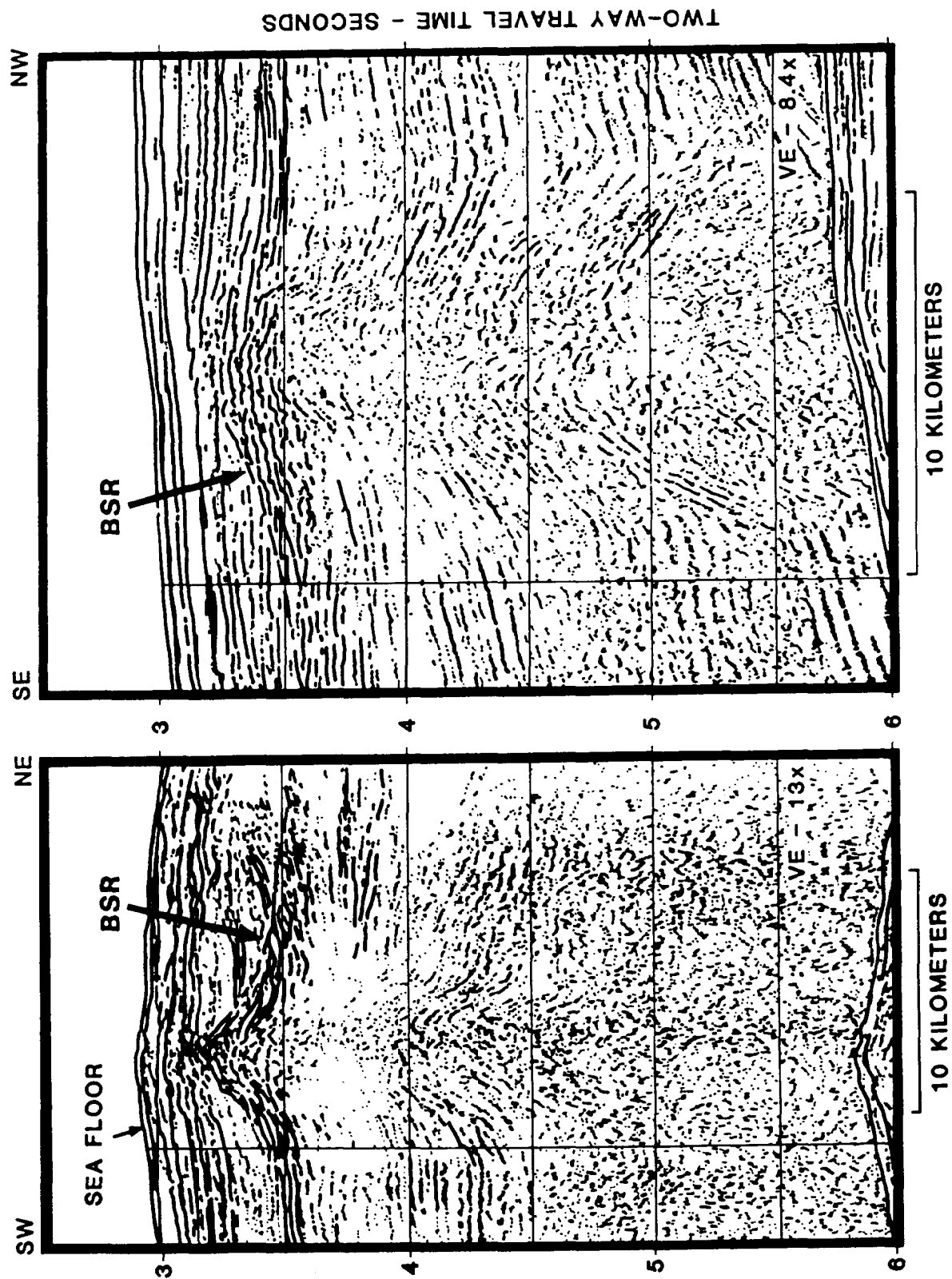
Figure 12. RELATION BETWEEN BOTTOM SIMULATING REFLECTORS (BSR) AND SALT DIAPIRS AT BLAKE OUTER RIDGE

After Paull and Dillon (1981)

from either: 1) a physical raising of the BSR as a result of salt intrusion, local disturbance of the sediment bedding reflectors is evident on the seismic sections, or 2) a physico-chemical readjustment of the BSR in response to changed temperature conditions following salt intrusion. An analysis of the thermal regime of salt diapirs by Keen (1983) suggests that the increased temperature above the top of the diapir (due to the high thermal conductivity of salt) together with convective temperature increases (due to migration of hot fluid up the sides of the diapir) would be sufficient to affect hydrate stability. The perturbations are on the order of 250 m, requiring an increase in local temperature of about 1 - 1.5°C.

Formation of Gas Hydrates in Sediments

General Requirements

The formation of gas hydrates in sediments initially requires the following:

1. The presence of a gas phase. In most cases the gas phase is dominantly methane but includes minor amounts of ethane, butane, pentane, carbon dioxide, hydrogen sulfide and possibly nitrogen.

2. The presence of a liquid phase. In the offshore environment this phase will be seawater at shallow sediment depths, but some chemical alteration may occur if diagenesis is important with burial, e.g. formation of carbonate and clay cements. The seawater needs to be at least saturated with the gas.

3. Appropriate conditions of temperature, load pressure, and vapor pressure to stabilize the gas hydrates (Figure 13).

Each of these requirements has other geological implications. For instance, the presence of light hydrocarbon gases requires organic matter in the sediment and sufficiently anoxic environmental conditions to guarantee organic matter preservation. Likewise, the generation of hydrocarbons from organic matter requires either microbial activity resulting in organic matter alteration and principally methane production and/or sufficient burial to thermally mature organic matter and produce light hydrocarbons.

The intensive chemical parameters are determined, at least in the offshore environment by bottom water temperature (a function of water depth, Figure 13), thermal gradient through the sediment, deposition rate, compaction rate, etc.

Thus, the stabilization of hydrates requires the input of specific materials and appropriate physico-chemical conditions. Apparently, such conditions have been met and maintained at the Blake - Bahama Outer Ridge because gas hydrates have been sampled and indirectly identified over a wide area. It is therefore instructive to examine the relative importance of individual stabilizing parameters in the framework of our present knowledge of the geology of this region, i.e. an attempt to put such parameters in a geological context.
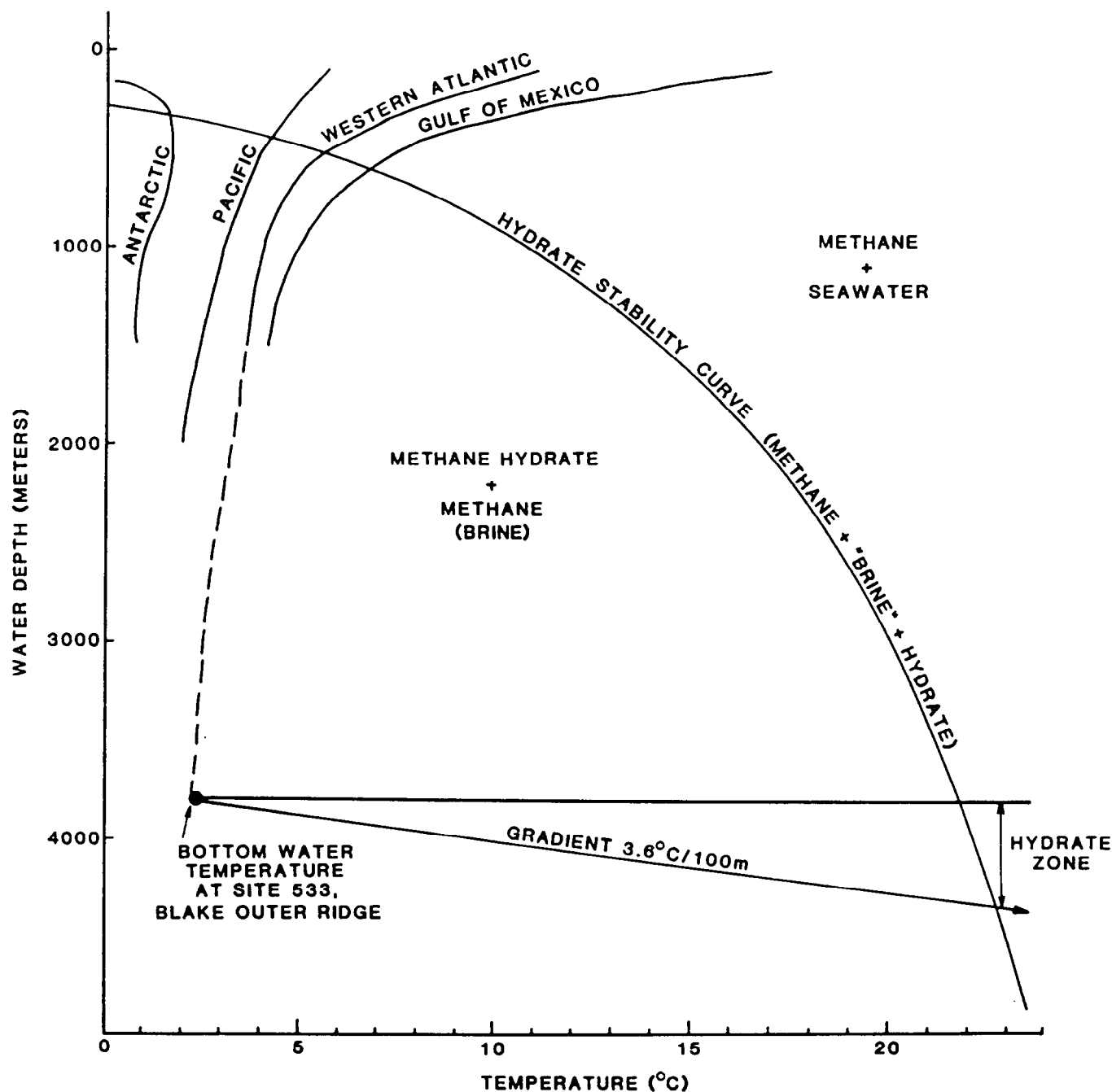
Figure 13. PHASE RELATIONS IN THE METHANE-SEA WATER SYSTEM AS A FUNCTION OF TEMPERATURE AND WATER DEPTH (assuming pressure gradient of 10.1 KPa/m)

The divariant assemblages methane hydrate + methane or methane hydrate + brine are stable in gas-dominated and water-dominated pore systems, respectively. Also shown are the temperature variations with water depth for Antarctic, Pacific, Western Atlantic, and Gulf of Mexico. The Western Atlantic curve is extrapolated to the depth of the Blake Outer Ridge using the algorithm in Tucholke et al. (1977). The steady state geothermal gradient at DSDP Site 533 assumed to be 3.6°C/100m.

Phase Relations in the Gas Hydrate System

The phase relations in gas hydrate systems are of fundamental importance in understanding the formation and stabilization of hydrates in the geological environment. Phase diagrams for a wide variety of hydrocarbon gases have been published, including those for methane hydrate (Roberts et al., 1941; Katz et al., 1959), ethane hydrate (Roberts et al., 1941; Deaton and Frost, 1938), propane hydrate (Frost and Deaton, 1946; Robinson and Mehta, 1971), and butane hydrates (Wilcox et al., 1941). Similar phase diagrams have been published by Kuuskraa et al. (1983).

In the offshore environment where temperatures are above 0°C the vapor pressure curve for hydrate formation (Figure 14) is commonly referenced in recent literature discussing hydrates in the geological environment (Tucholke et al., 1977; Claypool and Kvenvolden, 1983). The vapor pressure curves for hydrocarbon hydrates may also be obtained on the basis of thermodynamic calculations using the function $P = exp(a+b/T)$ or more complicated functions (Makogon, 1978) and using empirically derived constants (Smyth, 1970; Makogon, 1978; Kuuskraa et al., 1983).

In pure systems, e.g. CH_4 - H_2O, the phase relations are straightforward. Along the hydrate vapor pressure curve hydrates may exist in the presence of both gas and water. An increase in temperature causes the hydrates to dissociate and gas-saturated water exists with the gas. A decrease in temperature leads to the loss of a phase and the hydrates exist in the presence of either a gas in gas-dominated systems or water in water-dominated systems.

In the offshore environment, the equilibria are more complicated because the water is seawater. An added complication is the "salting-out" character of gas hydrate crystallization which excludes impurities, e.g. NaCl, from the hydrate lattice resulting in a coexisting liquid of brine rather than seawater composition.

Simplistically, the natural system can be approximated by the system CH_4 - H_2O - NaCl. The phase relations along the vapor pressure "curve" are hydrates + gas + brine representing a divariant equilibrium. Consequently, the vapor pressure "curve" is really a surface whereby the divariant phase relations can be maintained by varying two of the three parameters, temperature, pressure or fluid composition. In the trivariant equilibrium hydrates + brine there may be a wide variation in temperature, pressure and fluid chemistry over which the phase assemblage may exist.

The phase relations are illustrated schematically in Figures 15A and B. Figure 15A indicates the relations for a static pore system within the pressure and temperature zone of hydrate stability limited by the vapor pressure surface. The latter is an extension of the P - T vapor pressure curve into fluid composition space (X). In reality the surface may be geometrically complex. A pore fluid of seawater composition (B) lies on the intersection of an isotherm (vertical plane) and an isobar (horizontal plane). During gas hydrate crystallization under these conditions the hydrate has the gas free composition (H) and the pore fluid becomes progressively more saline along the line a-d.

Figure 15B indicates the relations for a dynamic pore system in which the sediment moves through pressure (P) and temperature (T), and fluid composition (X) space in response to the burial history. The pore system is constrained by the geothermal gradient surface. A fluid of composition b
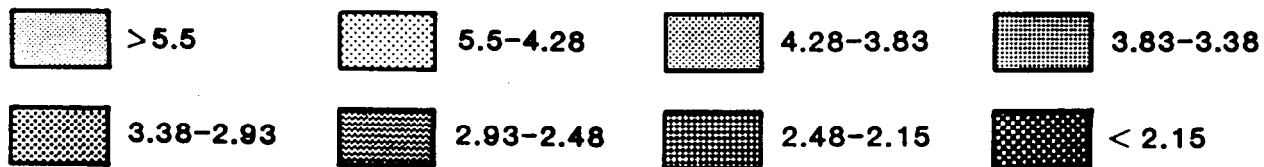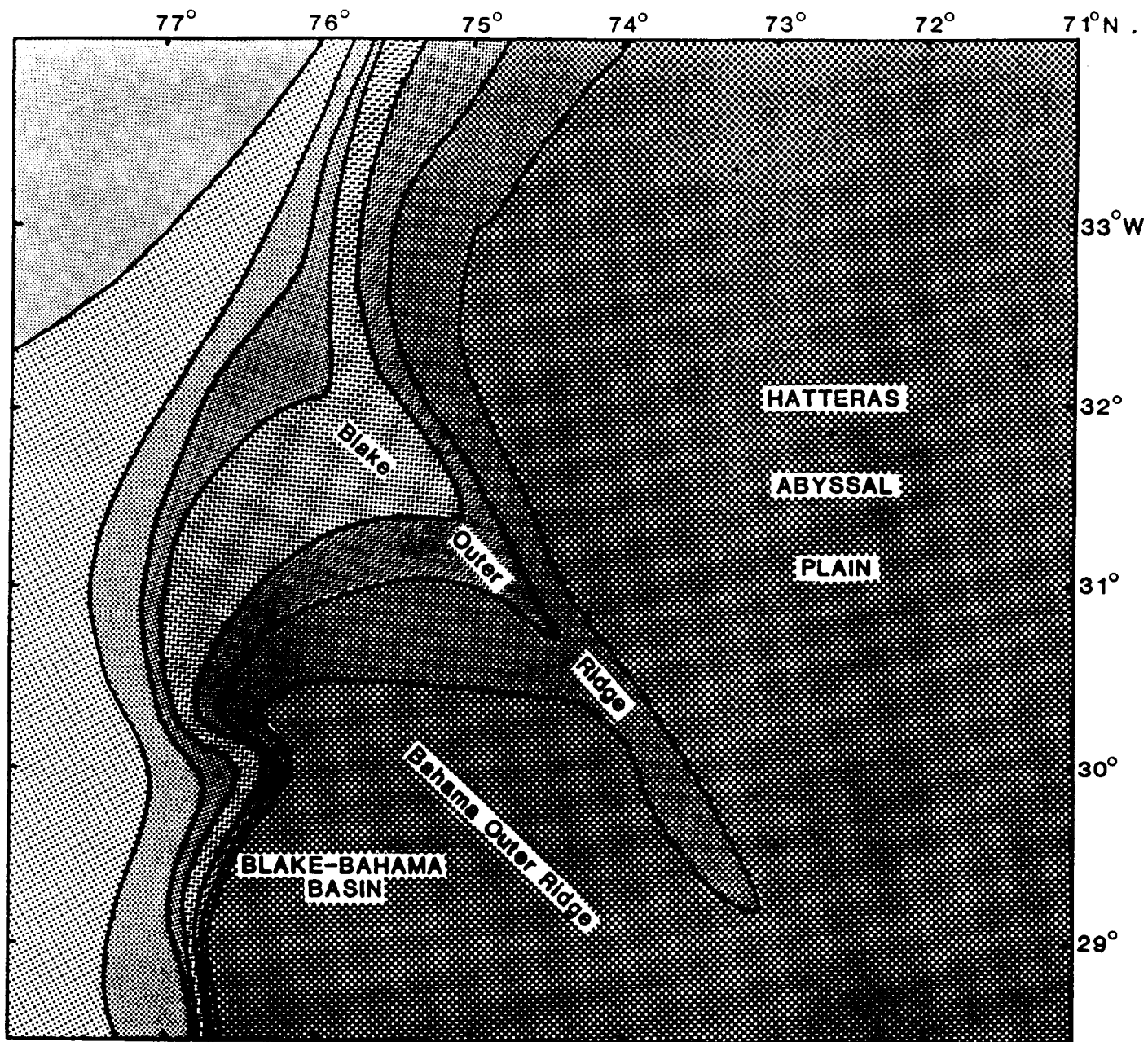
Figure 14. DISTRIBUTION OF BOTTOM-WATER TEMPERATURE IN °C IN THE BLAKE-BAHAMA OUTER RIDGE REGION

Determined by algorithms in Tucholke et al. (1977)
and a limiting temperature of 2.15°C

Figure 15A. P-T-X DIAGRAM FOR GAS HYDRATE STABILITY SHOWING ISOTHERMAL/ISOBARIC CONDITIONS EXPECTED IN A STATIC PORE SYSTEM

**Figure 15B. P-T-X DIAGRAM FOR GAS HYDRATE STABILITY
SHOWING POLYTHERMAL/POLYBARIC
CONDITIONS EXPECTED IN A DYNAMIC
PORE SYSTEM**

initially crystallizes hydrate h_1. The fluid composition evolves along the line b_1 - b_4 until at point X the geothermal surface intersects the vapor pressure surface and the hydrate h_x dissociates. This w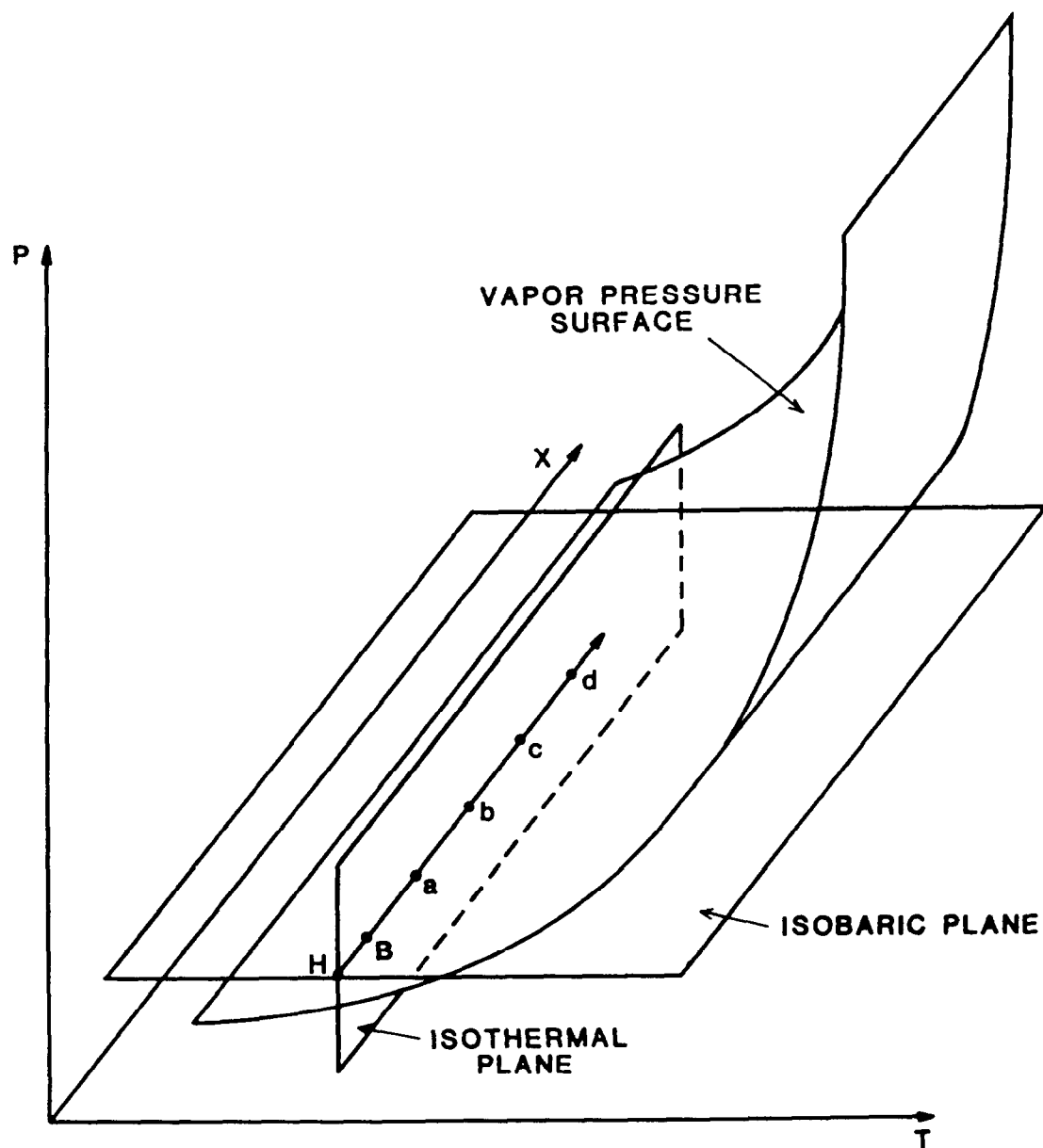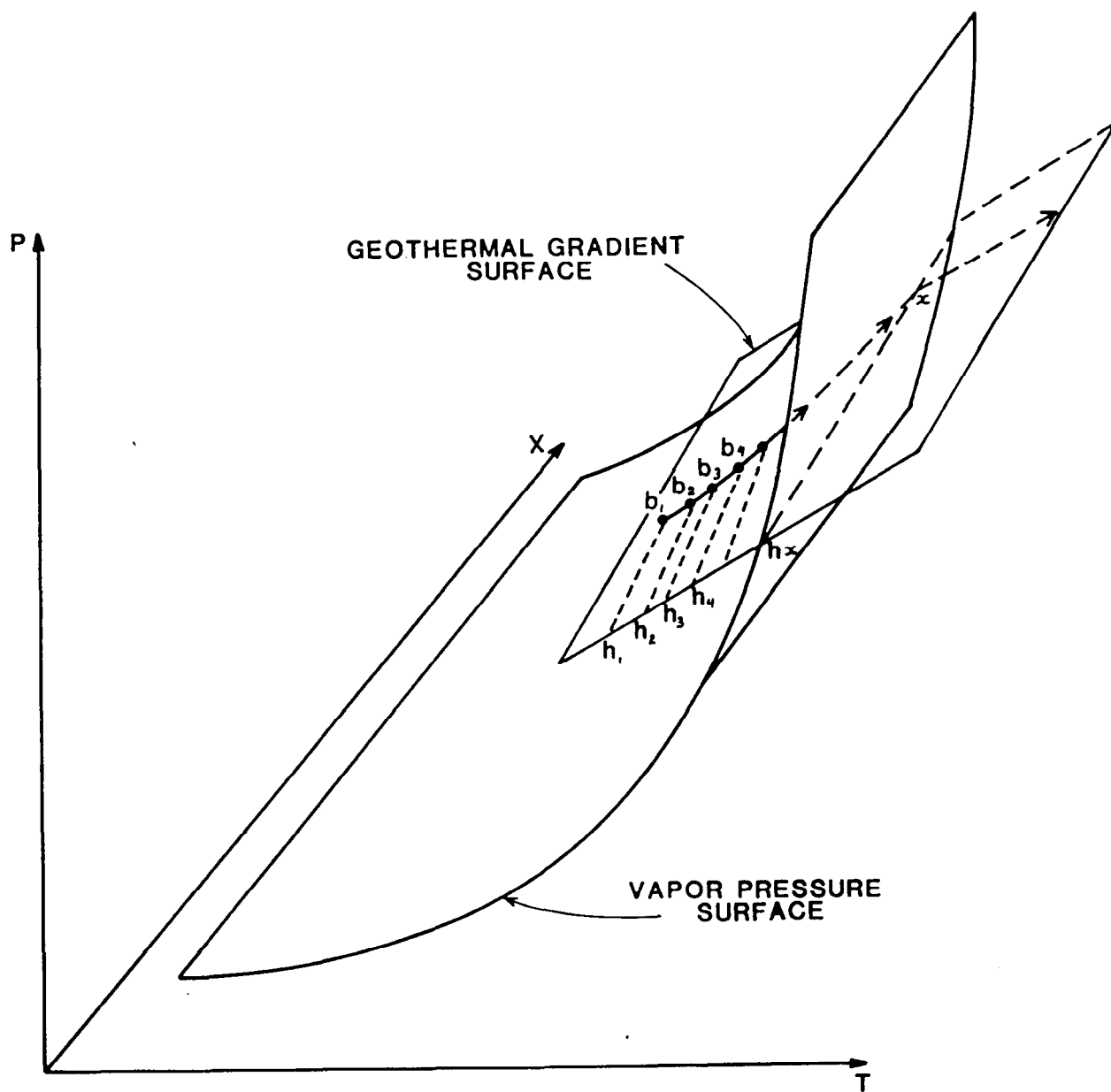ould represent the lower hydrate boundary. Evolution of the pore fluid beneath this zone would involve diagenetic mineral reactions but not include a hydrate phase.

With regard to the geological conditions at the Blake - Bahama Outer Ridge, it is reasonable to assume that the shallow sedimentary section is a water-dominated pore system. Thus, under ideal equilibrium conditions the major part of the sea floor BSR section should be a hydrates + brine system in which the volume of hydrates is determined by the volume of gas initially available (in a closed system) or by the time-integrated volume of gas generated and trapped (in a system open to gas). If the volume of hydrates crystallized is small then the residual brine will still approximate the composition of seawater, e.g. 20% conversion of seawater to hydrates leaves a residual brine with only 4.4% NaCl. Hence, in estimating hydrate zone thickness it is reasonable to use the methane + seawater stability curve if the volume of hydrates is relatively small.

However, given that at any depth in the section the temperature is fixed under steady-state thermal conditions, then the composition of the fluid phase may vary over a wide range while temperature and pressure are fixed, the extent of the variation being determined by the bulk composition of the system. In a water-dominated closed system presumably the volume of hydrates crystallized is small, so that the situation described above would prevail. In a water-dominated open system in which the gas phase is continuously replenished, the volume of hydrates crystallized is largely determined by the initial pore volume of water available; and the residual brine would be highly concentrated, e.g. 90% conversion of seawater to hydrates produces a residual brine with 35% NaCl. Under these circumstances, it would be inappropriate to use the methane + seawater stability curve, in that this curve would overestimate the thickness of the hydrate zone.

The presence of a gas-dominated pore system beneath the gas hydrate zone has implications for hydrate formation in the situation where the hydrate boundary moves downward, i.e. in areas where erosion has occurred. The gas-dominated pore system defines the underlying gas reservoir, beneath which the pore system becomes water-dominated. If the gas reservoir moves into the stability field of hydrates, then hydrates will crystallize, but the amount is determined by the availability of pore water, i.e. at irreducible water saturation the amount of hydrates crystallized would be small. Also, the system will be effectively closed because gas-filled pores prevent the movement of water into the reservoir. Beneath the gas reservoir, hydrate growth is facilitated again by the water-dominated pore system. Thus, the original hydrate "base" (possibly enriched in hydrates) is preserved within the stability field as a "stranded" zone. Beneath this exists a zone of minimum hydrate formation (the original gas reservoir) composed of hydrates + gas, and beneath this zone may be the new hydrate base located in the water-dominated pore system. As previously mentioned, such a vertical distribution of hydrate zones may produce the double reflections observed on the Blake - Bahama Outer Ridge flanks and which appear to correlate with surface erosion (Paull and Dillon, 1981).

Finally, the phase relations we have outlined above have been discussed with regard to methane hydrate stability, although it was noted that small

amounts of higher molecular weight gases are present at the Blake - Bahama Outer Ridge (Kvenvolden and Barnard, 1983). Those gases heavier than i-C$_4$ do not form hydrates, therefore are not considered in the phase relations discussed above. Nonetheless, in terms of the total phases these heavier gas species will be present but chemically inert, e.g. the trivariant equilibrium discussed of hydrates + water may actually be hydrates + water + heavier gases.

Gas Hydrate Nucleation and Crystallization

Experimental data indicate that natural gas hydrates do not grow spontaneously in the hydrate stability field once the fluid phase is gas saturated (Makogon, 1978) because of a strong kinetic effect. Under conditions of gas saturation, hydrate nuclei are unable to grow; a supersaturated condition must be attained in order to promote nucleation and crystal growth. The schematic conditions are shown in Figure 16. Two important equilibrium states are shown, the metastable equilibrium and labile (unsteady) equilibrium states. In the former, nucleation is energetically possible but not guaranteed; in the latter nucleation is ensured, but requires a greater degree of supersaturation. The change from metastable to stable equilibrium crystallization can only be achieved via the labile state (Figure 16). The relations shown in Figure 16 indicate that a fluid at A exists in the stable state if undersaturated with respect to some component, e.g. methane. Either cooling or decomposition of the fluid causes saturation at C; but hydrate nucleation will not begin until a critical level of supersaturation is reached, either in the metastable field (D) or labile (unstable) field (B). This situation is commonly observed in transport pipelines with respect to hydrate crystallization, but is not generally applicable to hydrate formation in sediments. More relevant is the condition where the P-T-X pathway is from A to B (Figure 16), i.e. an isothermal-isobaric condition. Here, the fluid also passes into the metastable field at C' to D, prior to hydrate nucleation. If nucleation and crystallization proceed in the metastable state, either a further increase in temperature or further supersaturation are necessary to promote the stable equilibrium condition. Such an increase in temperature may be brought about by burial but will also be accompanied by an increase in natural gas solubility. This may have two effects. Firstly, as long as the new solubility conditions can be met, pores already containing hydrate crystals will continue to grow because of a seeding effect. Secondly, pores without hydrates will not nucleate hydrate crystals without going through the supersaturation conditions described above. Because the solubility has increased, the degree of supersaturation may also be greater. As the sediment is buried, the hydrate zone develops to the limiting temperature and pressure conditions of hydrate stability. During this process the distribution of hydrates through this zone will generally be heterogeneous and determined by the rate of nucleation and crystal growth. This, in turn, is determined by the extent to which pores containing fluid, but free of hydrates, can be supersaturated with the gas phase. Once the hydrate zone is established the further nucleation and growth of hydrates will be determined by the availability of gas in a water-dominated pore system. This availability is dependent on the presence of a source of biogenic gas, i.e. organic material, and sufficient permeability to distribute the gas.
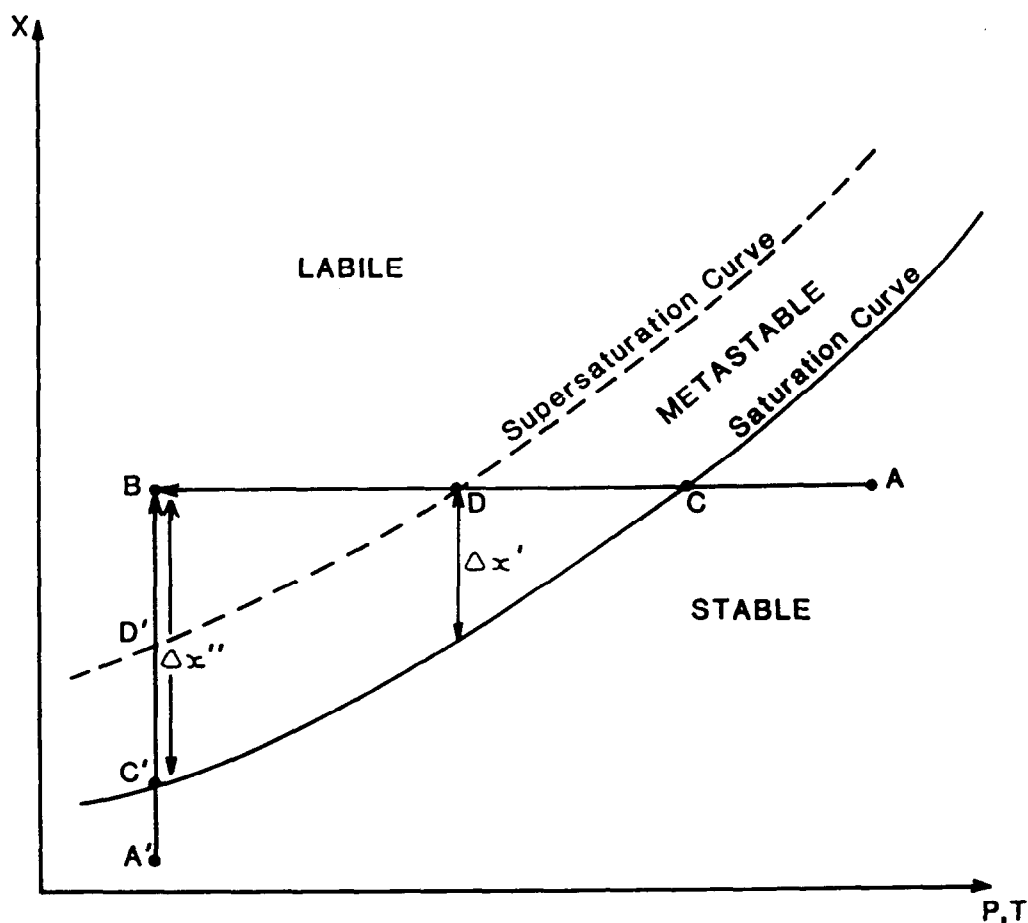
Figure 16. SCHEMATIC DIAGRAM OF EQUILIBRIUM RELATIONS IN A TYPICAL GAS-WATER-HYDRATE SYSTEM

The stable, metastable and labile areas in a plot of fluid compositions (X) versus pressure (P) or temperature (T). A fluid at A is decompressed or cooled through the saturation point (C) and may nucleate crystals at D or within the labile field at B. At D, the degree of supersaturation is $\Delta x'$, and at B is $\Delta x''$. For the case of a pore system at constant pressure and temperature (A'), the fluid nucleates at D' or perhaps at B where the degree of supersaturation is given $\Delta x''$.

The sediment permeability is partly determined by the growth of hydrates. In a pore system containing both gas and water, capillary pressure forces the water into the pore throats and a curved miniscus surface exists between the gas and water phases. According to the experiments of Makogon (1978), initial hydrate nucleation occurs at this interface where supersaturation conditions are optimal. Hydrate growth is then controlled by a "volume diffusion" mechanism whereby growth rate is controlled by the rate of diffusion of gas through the hydrate layer to the water-hydrate interface. In this manner both gas and water are expended and hydrates are produced. The initial distribution of water in the pore throats determines that as the hydrates grow the pore throats will be gradually blocked, hence the sediment permeability will be severely reduced. The growth of hydrates may then be limited by the development of impermeability to gas migration. This condition may easily develop in the fine-grained sediments of the Blake - Bahama Outer Ridge where even the initial permeability is probably much less than 1 md.

Gas Solubility and Hydrate Formation in Clayey Sediments

We have previously indicated that the phenomenon of undercooling in hydrate systems suggests that supersaturation is a necessary condition for hydrate nucleation. In kinetic terms, the rate of gas solution is greater than the rate of crystal nucleation. Although we do not know the extent of super-saturation required to promote hydrate nucleation, the degree is related to the gas solubility, higher solubility requiring a greater degree of supersaturation.

It is therefore pertinent to inquire about the solubility of hydrocarbon gases in pore fluids trapped within clayey sediments and also the structural conditions of such fluids. Solubility data discussed in the literature commonly reference laboratory measurements of hydrocarbon gases that show such gases are rather insoluble in seawater or brine because of a "salting out" effect (Long and McDevit, 1952). For instance, Rice and Claypool (1981) indicate methane solubility of 800 - 3,200 ppm in seawater, based on the work of Culbertson and McKetta (1951). The dominant effect on solubility is pressure.

Experimental data of gas solubility should be considered minimal values because in such experiments the gas-water interface is essentially flat. This interfacial condition cannot exist in a sediment with small pores where strongly curved interfaces exist between a free gas and a water phase. The curved boundary is maintained because the pressure within the gas phase is higher than within the water phase, and consequently the escaping tendency of gas is high (the Kelvin effect). This escaping tendency can be expressed in terms of gas solubility, and it increases as the interfacial curvature increases. The smaller the sediment pores, the greater will be the gas solubility. In a clayey sediment undergoing compaction the hydrocarbon gas solubility will increase with depth of burial as the porosity decreases from 70 - 80% to 35 - 40%, as observed for Blake - Bahama Outer Ridge sediments. During this compaction the solubility may increase by an order of magnitude, depending upon the molecular weight of the gas species.

Another important condition effecting hydrocarbon gas solubility is the structural state of the pore fluid. In sediment containing large pores and a low clay content, e.g. quartz sand, the pore water may be expected to be normal bulk water. However, a large number of investigations indicate that

near clay surfaces the pore water becomes more structured (Low, 1961; Barefoot and van Elsberg, 1975; Schwarzer, 1966; Burst, 1976) and differs from bulk water in terms of many properties, e.g. dielectric constant, freezing point, density, and thermodynamic properties.

Assuming that the clay component of clayey sediments is largely montmorillonite, then it appears that the structured water is less dense than bulk water (Anderson and Low, 1958). In simplistic terms, the water may be considered to have been "stretched" (in the sense used by Long and McDevit, 1952) and to contain "holes". Consequently, if a certain amount of energy is expended by a dissolving gas in order to push aside water molecules, then it follows that structured water already containing "holes" will be a more effective solvent for hydrocarbon gases permitting a higher concentration of gas in structured water adjacent to clay grains than in the bulk pore water.

Note also that the idea of structured water suggests a certain degree of molecular ordering similar to that observed in ice and in hydrates. Studies by Makogon (1978) have shown that hydrate crystallization is much enhanced by the presence of water already having some icelike structure, so we might expect that water in close proximity to clay surfaces would be potential sites for hydrate crystallization. As compaction proceeds the pore spaces are progressively reduced and the volume of water in close proximity to clay surfaces increases. The volume of structured water will then progressively increase with depth, facilitating the crystallization of hydrates.

The Availability of a Gas Phase During Hydrate Formation

In our introductory remarks, we noted that a prerequisite for gas hydrate formation is the presence of a free gas phase, with the implication that the coexisting fluid phase is saturated or supersaturated with respect to the gas. When discussing the gas phase, we require the presence of one or more gas species which may be incorporated into the hydrate structure (C_1 - C_4). Other gaseous species ($>C_4$) may be present but are not important with regard to hydrate equilibrium unless their partial pressures make a significant contribution to the total gas pressure.

In marine sediments the ultimate source of gaseous hydrocarbons is organic detritus deposited with clastic material at the sediment-water interface and then buried. A recent review by Claypool and Kvenvolden (1983) illustrates the processes whereby organic material is progressively altered by either biological or thermal processes with the release of hydrocarbon gases. In both processes the dominant gaseous product is methane. In the case of microbial alteration, methane is accompanied by only trace amounts of higher molecular weight hydrocarbons (mainly C_2 - C_4). The origin of these gases may also be determined by their carbon isotopic compositions.

At the Blake Outer Ridge hydrocarbon gases were collected to a depth of 392 m and analyzed in detail (Sheridan et al., 1983; Kvenvolden and Barnard, 1983; Galimov and Kvenvolden, 1983; Claypool and Threlkeld, 1983). Free methane, ethane, propane, iso- and n-butane, iso- and n-pentane, iso- and n-hexane were all found. Methane is 3 orders of magnitude more abundant than the other gases but the general trend is toward C_1/C_2 decrease as a function of depth. Near-surface scatter of C_1/C_2 ratio is probably due to diffusional loss of methane across the sediment-water interface. The C_1/C_2 decrease is similar to that observed at other DSDP sites and suggests an increasing component of heavier thermogenic gas (C_2 - C_6 content is greater

and the ratio of iso- to n-hydrocarbons decreases in deeper samples). Overall high C_1/C_2 ratios of $>10^4$ are consistent with biogenic methane being the dominant gaseous species. These conclusions are also consistent with carbon isotope measurements which show that $\delta^{13}C$ (CH) vary with depth from -94 to -66 per mil., $\delta^{13}C$ (CO_2) from -25 to -4 per mil., and $\delta^{13}C$ (organic) from -25 to -21 per mil. These measurements indicate CO_2 production from organic matter and subsequent reduction of CO_2 to CH_4 by microbial activity, but do not preclude methane production through other pathways, e.g. acetate reduction. In contrast with the free core gases, those analyzed from the recovered hydrate sample contain C_1 - C_4 species but no heavier hydrocarbons, which are prevented from entering the hydrate lattice.

The processes of fermentation and oxidation of organic matter to produce CO_2 and the subsequent microbial reduction to generate CH_4 proceed only under anoxic conditions and in the absence or dilute concentrations of dissolved sulfate in the pore fluid. This latter conditions exists at DSDP Site 533 within the top 14 m of sediment so that CH can potentially be generated from this depth downwards. Removal of sulfate from the pore fluid also implies anoxic conditions because sulfate-reducing bacteria also require an organic matter substrate for the process to proceed and anoxia guarantees initial organic matter preservation. The rapid removal of sulfate may be achieved if the sulfate-depleted pore fluid is not replenished with sulfate-rich bottom water diffusing downwards. Such a condition is most easily achieved if the sedimentation rate is relatively high, as seems to be the case at Site 533 (see below) and at other DSDP locations on the Blake - Bahama Outer Ridge.

The nature of the organic matter is also important in determining the amount of methane which may be generated during alteration. Generally, terrestrially derived (Type III) organic matter is gas prone relative to marine (Type I, II) organic matter (Rashid and Vilks, 1977) and a relatively large volume of methane can be produced from a small amount of terrestrial organic matter. At the Blake - Bahama Outer Ridge, the organic matter has not been characterized microscopically. However, Kvenvolden and Barnard (1983) report $\delta^{13}C$ values for separated organic matter of -25 to -21 per mil. suggesting the presence of a component of terrestrial plant material. If we assume that marine planktonic material in hemipelagic sediments has $^{13}C \cong$ -18 per mil. (Smith and Epstein, 1971) and that plant material has $^{13}C \cong$ -27 per mil., then the measured $\delta^{13}C$ values at the DSDP Site 533 indicate a terrestrial organic carbon component of 30 - 80% (Note: These figures must be treated with caution. The carbon isotope compositions of land plants and marine materials are determined by many factors and cover a range of values. Nonetheless, isotopic compositions approaching -25 per mil. imply a component of terrestrial origin). Hence, parts of the sedimentary column may be prone to methane production. Brooks et al. (1983) also indicate mixed marine-terrestrial organic material.

At DSDP Sites 102, 103, 104, and 533 the organic carbon content of the sediments has been determined on a weight percent basis (Kvenvolden and Barnard, 1983; Sheridan et al., 1983b; Boyce, 1972). Using this data, average total organic carbon (TOC) values have been calculated (Table 4). Because there is a dilution effect due to the presence of authigenic carbonate, the values are shown both uncorrected and corrected for carbonate content.

TABLE 4.

ORGANIC CARBON CONTENT IN SEDIMENT AT DSDP SITES 102, 103, 104, 533

Site 102	Uncorrected %	Corrected %	No. of samples
Pleistocene-Holocene	0.77	0.94	41
Pliocene	0.80	0.98	27
Late Miocene	0.80	0.92	9

Site 103	Uncorrected %	Corrected %	No. of samples
Pleistocene	0.10	0.15	2
Pliocene	0.38	0.45	7
Late Miocene	0.99	1.12	7

Site 104	Uncorrected %	Corrected %	No. of samples
Pleistocene	0.32	0.42	4
Late Miocene	0.60	0.67	14
Late-Middle Miocene	0.93	1.06	16
Early-Middle Miocene	0.91	1.15	8

Site 533	Uncorrected %	Corrected %	No. of samples
Pleistocene	0.68	0.91	29
Late Pliocene	0.40	0.60	1
Middle-Late Pliocene	0.98	1.14	14
Early Pliocene	1.10	1.32	31

Because the organic carbon content, measured as weight percent, is sensitive to the accumulation rate of clastic sediment, it is difficult to evaluate the relationship between fluxes of organic matter and sediment on this basis. Instead, the sediment fluxes are calculated in terms of $mg/cm^2/year$, which allows for direct comparison of clastic and organic material fluxes. At the four DSDP sites, the clastic sediment fluxes were calculated using a grain density of 2.65 g/cm^3, measured depth-porosity relations, and stratigraphic thicknesses shown in the DSDP Initial Reports. From the clastic flux, the flux for organic carbon can be calculated from the measured percentage data. Results of these calculations are shown in Table 5.

TABLE 5.

CLASTIC/ORGANIC FLUXES AT DSDP SITES 102, 103, 104, 533

| Site/Time Span	102	103	104	533
Pleistocene-Holocene	15.5/0.15	14.3/0.02	2.38/0.01	9.9/0.09
Pliocene	15.5/0.15	14.3/0.06	n.d.	13.4/0.17
Lower Miocene	4.96/0.05	7.15/0.08	2.38/0.015	n.d.
Middle Miocene	n.d.	n.d.	14.3/0.15	n.d.

n.d. = no data available
Rates are in $mg/cm^2/year$

- 58 -

These data are shown in a little more detail in Figures 17 A - D in which the organic flux is compared to the clastic sediment flux. The sediment fluxes are abnormally high for the slope and rise region, an observation consistent with the proposition that the Blake - Bahama Outer Ridge was built through deposition from a current system abnormally laden with sediment. Also, the organic carbon flux is positively correlated with the sediment flux, excepting Site 103 where the correlation is negative.

The relations of Site 103 suggest a different depositional history for this part of the ridge. Possibly the sediment source was distinct at Site 103. Note that the organic flux is significantly lower at Site 103 compared to the other DSDP sites, although the cored sediments were described as "gassy" in the Leg 11 Initial Report. It would be interesting to ascertain if hydrates occur at this site which appears to be close to the southern limit of hydrate presence according to the BSR map of Paull and Dillon (1981). The negative flux correlation observed at Site 103 cannot be a simple clastic dilution effect, because the organic flux varies by almost an order of magnitude in contrast to the much smaller variation in the clastic flux. It certainly appears that Site 103 was starved of organic matter compared to the other ridge areas. We would suggest that if Site 103 is devoid of hydrates, then the observed organic flux provides an approximate lower limit for hydrate formation, i.e. below approximately 0.1 mg/cm^2/year, the organic flux is insufficient to provide enough methane for hydrate formation.

These observations have implications for the generation of hydrocarbon gases subsequent to sediment deposition. The flux of organic matter into the sediment column is not particularly high, suggesting that either productivity was low or the water column was sufficiently oxygenated to destroy most of the organic matter during transport to the sea floor. Given that at least part of the organic matter may have been originally deposited on the Blake Plateau, remobilized and redeposited at the Blake - Bahama Outer Ridge, the residence time in the water column may have been sufficiently long to facilitate oxidation. Nonetheless, once the organic matter was deposited, its preservation must have been aided by the relatively high flux of clastic material. Under such conditions, downward diffusion of oxygen-bearing bottom water into the shallow sediment column is reduced and hydrogen sulfide rapidly accumulates due to microbial sulfate reduction. The result is the development of anoxia at shallow depths in the sediment column. This condition is also suggested by the rapid removal of sulfate from the pore fluid at DSDP Site 533 (Sheridan et al., 1983), within 14 m of the sediment-water interface.

There are several specific controls on the organic content of sediments. Probably the major control is clastic flux (sedimentation rate); its control on redox conditions has been described above. Thus, rapidly deposited sediments contain the highest TOC in generally oxidizing offshore environments. Usually this level is 1 - 1.5% maximum because of the destruction of organic matter in the water column. TOCs also tend to be higher in fine-grained muds simply because the physical conditions of transport concentrate low density organic matter into this fraction. In reducing environments the TOC is inversely related to clastic flux, in contrast to the situation in oxidized environments. This relation results because the chemical conditions facilitate
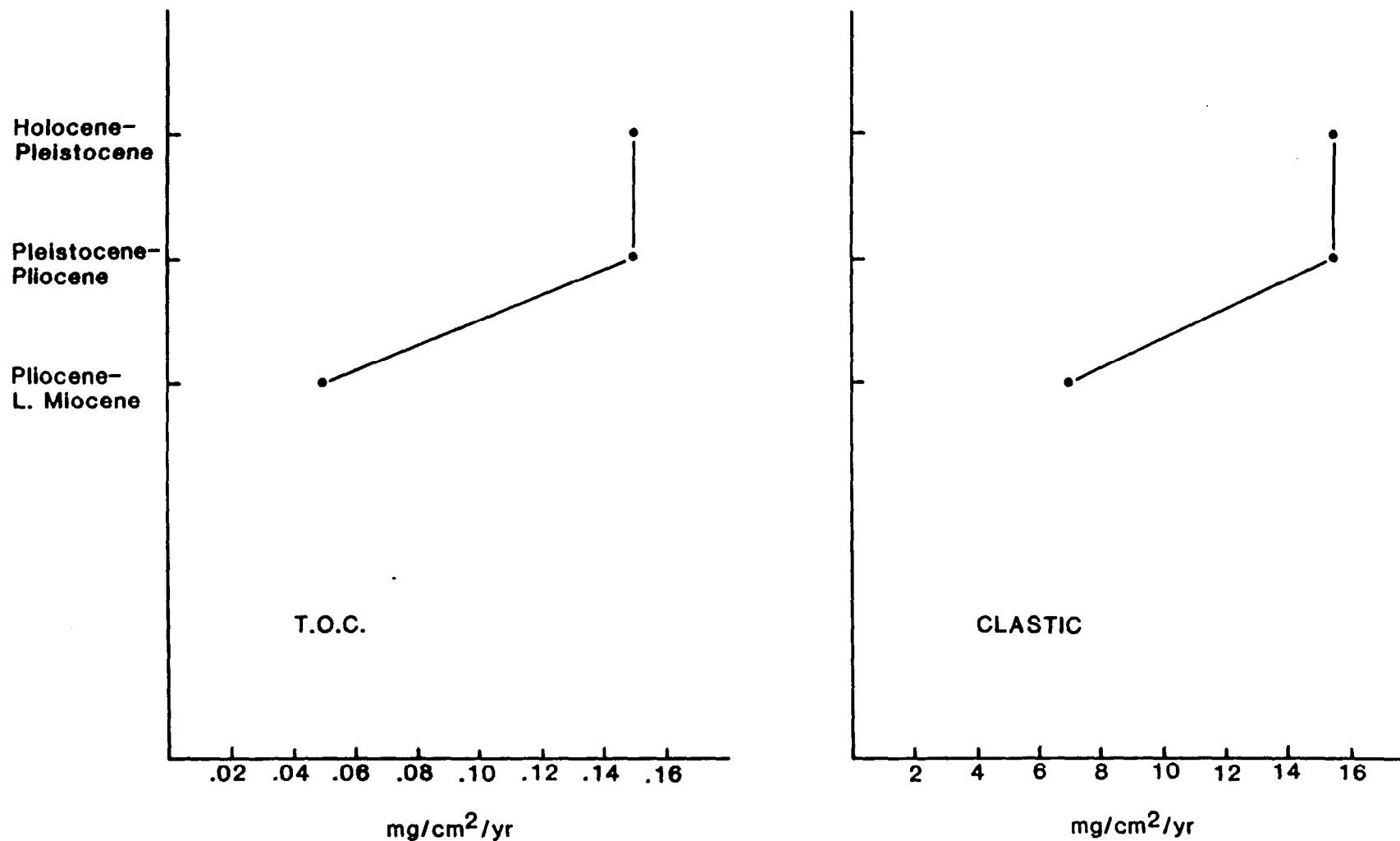
Figure 17A. FLUX OF ORGANIC AND CLASTIC MATERIAL AT DSDP SITE 102
BLAKE OUTER RIDGE

Calculated on a carbonate-free basis, from DSDP Leg 11 Initial Report, assuming a clastic density
of 2.65 g/cm^3, and initial porosity of 55%.
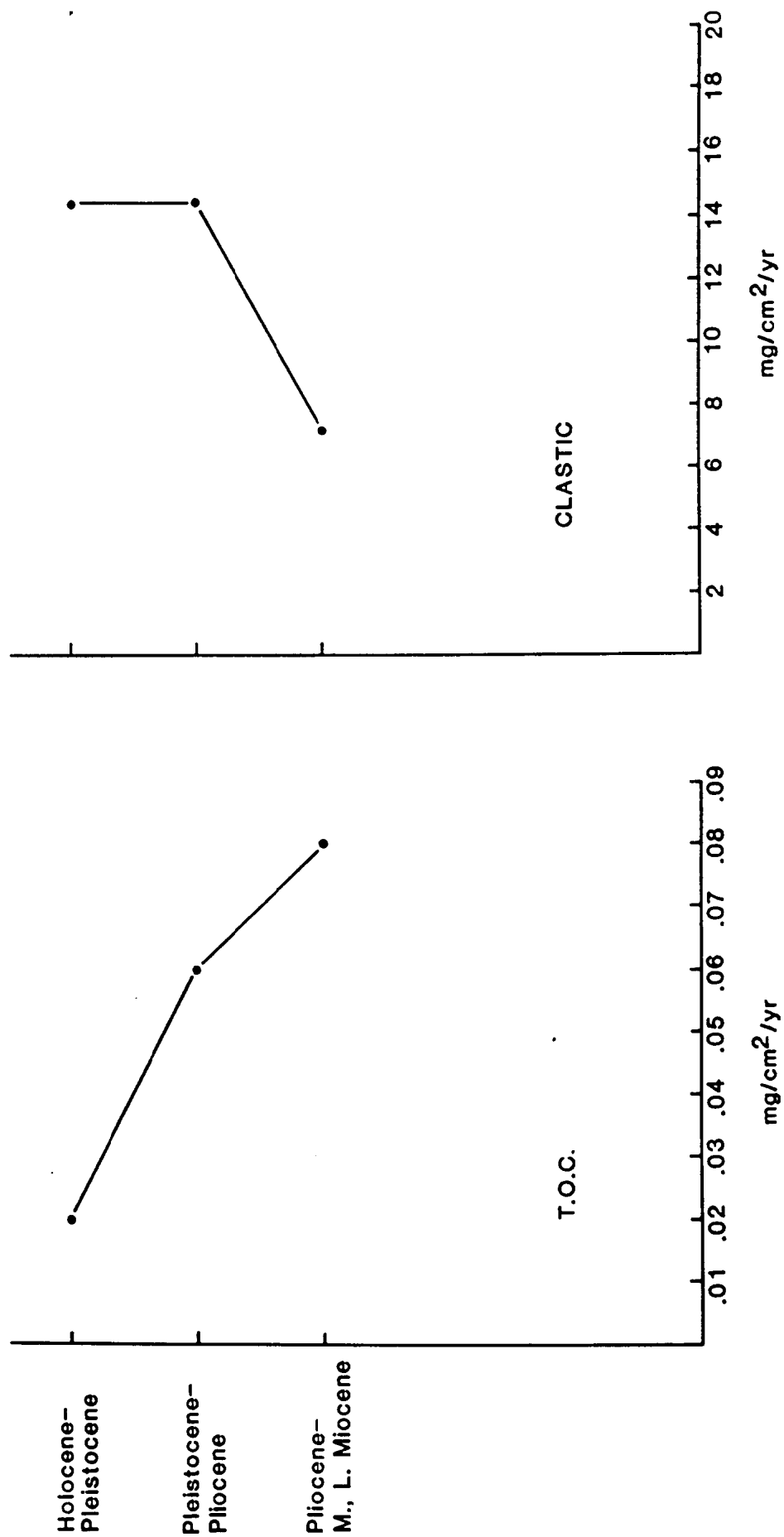
Figure 17B. FLUX OF ORGANIC AND CLASTIC MATERIAL AT DSDP SITE 103 BLAKE OUTER RIDGE

Calculated on a carbonate-free basis, from DSDP Leg 11 Initial Report, assuming a clastic density of 2.65 g/cm³, and initial porosity of 55%.

Figure 17C. FLUX OF ORGANIC AND CLASTIC MATERIAL AT DSDP SITE 104 BLAKE OUTER RIDGE

Calculated on a carbonate-free basis from DSDP Leg 11 Initial Report, assuming a clastic density of 2.66 g/cm3, and initial porosity of 55%.
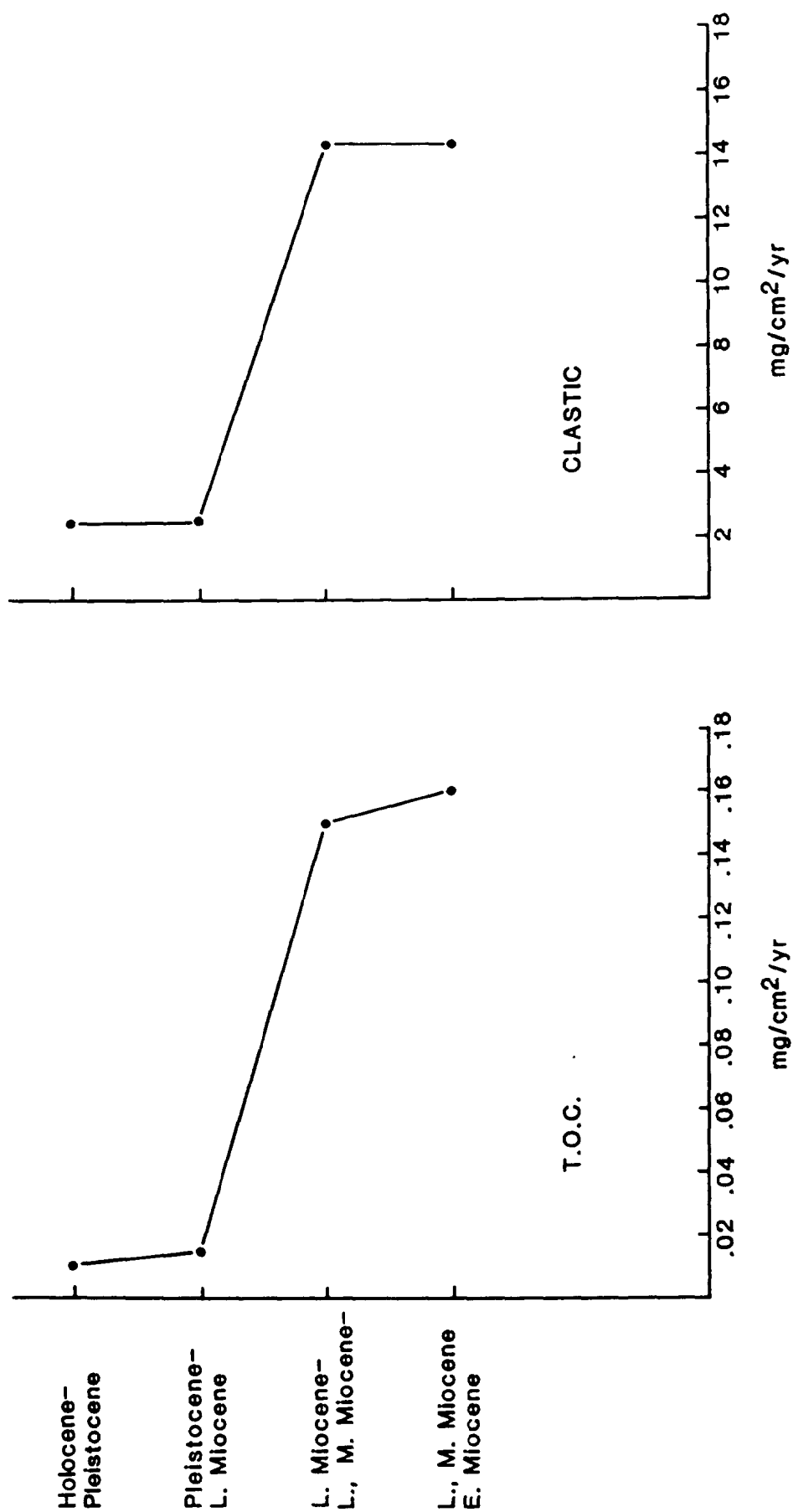
- 62 -

Figure 17D. FLUX OF ORGANIC AND CLASTIC MATERIAL AT DSDP SITE 533 BLAKE OUTER RIDGE

Calculated on a carbonate-free basis from DSDP Leg 11 Initial Report, assuming a clastic density of 2.65 g/cm³, and initial porosity of 55%.
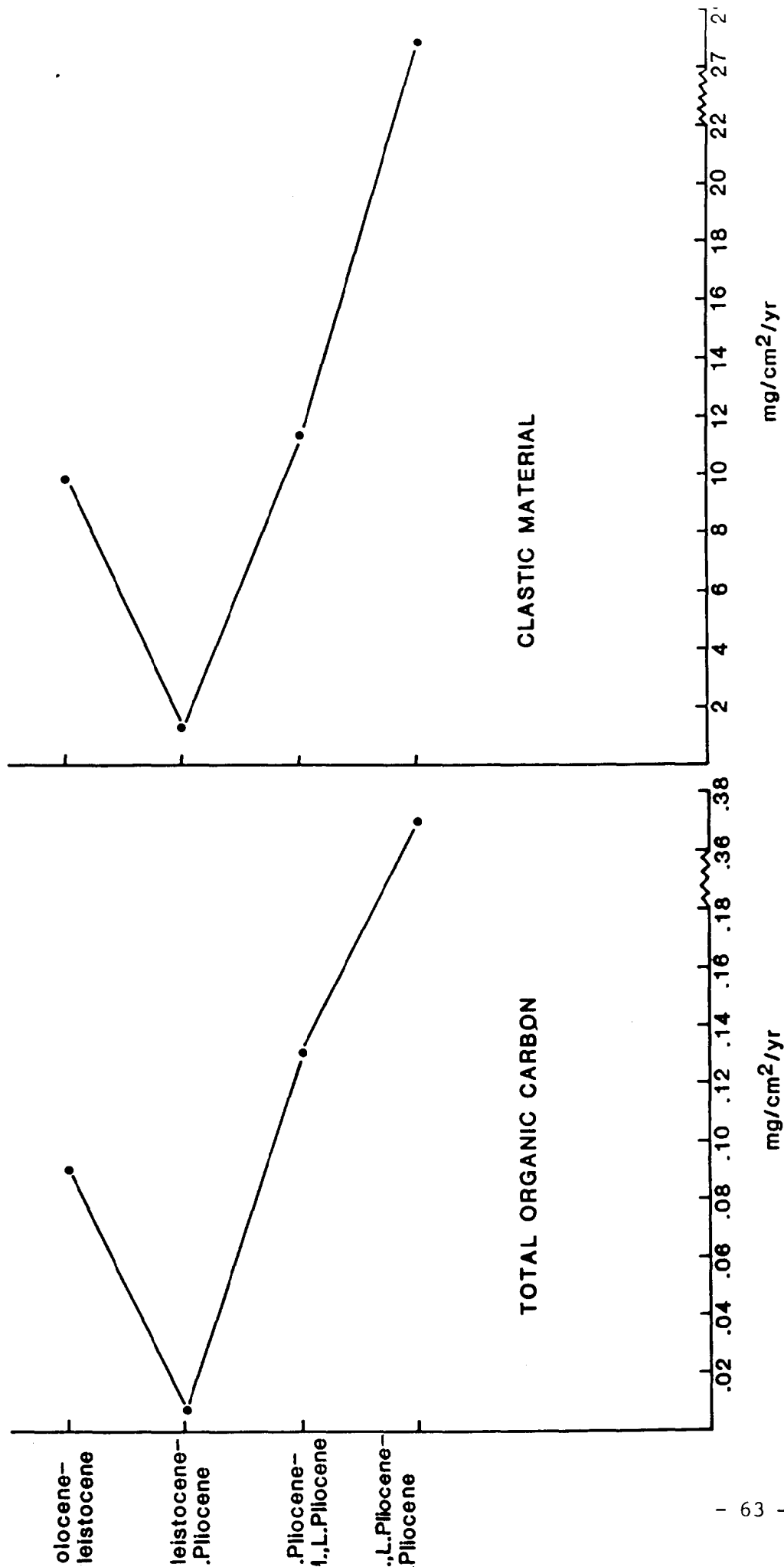
organic matter preservation and the high clastic flux has a simple dilution effect.

An additional factor is organic productivity, which is highest in regions of upwelling of nutrient-rich water. Upwelling generally occurs on the eastern margins of the major ocean basins and at middle latitudes. Not only does high productivity provide a rich source of potential organic carbon, but it also will remove oxygen from the water column during organic matter decomposition resulting in a strongly oxygen-depleted oxygen minimum. If the oxygen concentration falls below 1 - 1.5 ppm, then conditions are sufficiently reducing to preserve organic matter wherever the oxygen minimum impinges on the continental margin. A well-developed oxygen minimum exists along the eastern coast of the U.S., but contains more than 2.5 ppm oxygen. Consequently, such conditions lead to destruction rather than preservation of organic matter.

Thus, it appears that preservation of organic matter, i.e. high-TOC sediments, results from high surface productivity and reducing conditions in the water column. Under oxidizing conditions TOC may also be maximized if the clastic flux is high enough. These various conditions also appear to be related to sea level changes in that high-TOC sediments are produced during periods of marine transgression. At those times when climatic conditions have resulted in stagnancy and shallow epicontinental seas are present, then fine-grained, organic-rich sediments result.

How might these various considerations be evaluated in terms of the Blake - Bahama Outer Ridge? A complication arises because of the complexity of transport and deposition involving the outer ridge sediments. A major component of the sediment appears to have been derived from clastics previously deposited on the Blake Plateau, i.e. the sediments are reworked from older, fine-grained materials laid down in shallower water. In addition, there may be a component of sediment contributed by the western boundary undercurrent.

Nonetheless, some general conclusions may be drawn. Firstly, the preservation of organic matter is largely the result of a relatively high clastic flux. Secondly, it is unlikely that given the probable Tertiary age of the reworked sediment (the Tertiary section is much reduced on the Blake Plateau), and the geographic position, a strongly reducing environment existed during the evolution of the Blake - Bahama Outer Ridge. Thirdly, the positive correlation at three DSDP sites between organic and clastic fluxes supports a generally oxidizing environment above the sediment-water interface. Consequently, organic-rich muds are not to be expected anywhere in the region of the Blake - Bahama Outer Ridge. A fourth, very tentative conclusion may be reached. Except for Site 102, the trend is from a high flux of organic carbon, in the middle Miocene, to a lower flux in the Pleistocene. This trend may correlate with high stands of sea level during the middle Miocene and lower stands in the Pleistocene. Given, however, the complex depositional history and low resolution of the data, such a correlation requires further substantiation.

Thus, we have demonstrated that the preservation of organic matter at the Blake - Bahama Outer Ridge is largely controlled by a relatively high flux of clastic material. The absolute values of TOC flux are quite low (the muds would usually be classified as poor to moderate source rocks), and are predicted to be equally as low throughout the Blake - Bahama Outer Ridge region. The question then arises if such fluxes are sufficient to generate

enough methane to stabilize a gas hydrate. The minimum amount of organic matter required to support hydrocarbon production is a contentious subject. Values of 0.5 - 0.6% TOC are frequently referenced (Rashid and Vilks, 1977; Claypool and Kaplan, 1974), although the type of organic matter is probably as important as its absolute concentration. In general, we would expect that terrestrial organic material (herbaceous, coaly, and woody types) would largely be concentrated nearshore and such sediments would be prone to methane production. However, the Blake - Bahama Outer Ridge muds contain a significant component of terrestrial organic material despite the abyssal environment, so even here the organic matter mix is almost optimal for methane production.

We can roughly estimate the organic carbon requirements to produce enough methane to saturate the pore fluid, a minimum necessity to stabilize hydrates. We have previously estimated both organic and clastic fluxes at the Blake - Bahama Outer Ridge, but we also need to evaluate the fluid flux. This is more difficult because there is a flux out of the sediment during compaction. If we assume that the average porosity between the sediment-water interface and the limit of hydrate stability is 45%, and the average clastic flux is 12 mg/cm²/yr, then the average fluid flux is about 3.7 mg/cm²/yr. At 4,000 m water depth and at sediment depths of less than 600 m, the experimentally determined methane solubility is about 3,500 ppm. Therefore, in order to continuously saturate the pore fluid, a methane flux of .013 mg/cm²/yr is needed, which in turn requires an organic carbon flux of .01 mg/cm²/yr. Given that only a fraction of the TOC is converted to methane, then the necessary organic flux may be significantly higher than this value. Accepting that the calculated value of .01 mg/cm²/sec is crudely derived, it nonetheless implies that some of the sediments at the Blake - Bahama Outer Ridge are marginally capable of saturating the available pore fluid; and hence, hydrate crystallization may be severely restricted. This situation is exacerbated if a supersaturated condition is an initial requirement of gas hydrate nucleation. This conclusion is consistent with the calculations of only 1,600 ppm methane in pore fluid at Site 533 (Claypool and Threlkeld, 1983). Thus, we conclude that the apparently low volume percentage of hydrates at the Blake - Bahama Outer Ridge is compatible with the low flux of organic carbon.

Is there a condition by which the availability of methane can be increased? Eventually, the sediment column passes outside the stability field of hydrates. Any hydrate previously crystallized melts, releasing methane. If permeability permits, the methane ascends back into the hydrate zone, providing an additional supply for hydrate formation. This process begins and may be limited to the lower part of the hydrate zone because with hydrate growth, gas permeability will decrease with a consequent starvation of the upper hydrate zone.

### Pore Fluid Chemistry and Gas Hydrate Formation

There are a number of potential effects on pore water chemistry that are directly or indirectly associated with hydrate crystallization, some of which can be evaluated from pore fluid data at the four DSDP sites.

A major direct effect is expected to be an increase in pore water salinity as a function of the percentage of hydrates crystallized because of a

strong "salting-out" effect. In the absence of water convection, such salinity zones should indicate the presence of hydrates, although the magnitude of the salinity changes may be diminished due to diffusion. The chlorinity and salinity profiles at Site 533 are shown in Figures 18A and B. One explanation for the profile would be a progressive freshening of pore water between 200 - 380 m interrupted by two zones of anomalously high salinity (shaded in Figure 18A). The high salinity zones would then represent strongly saline fluids developed during hydrate crystallization that subsequently diffused into adjacent zones. The overall freshening trend suggests crystallization of less than 10% hydrates by volume in the pore spaces. Another possible interpretation is shown in Figure 18B where the "background" chlorinity profile shows a gradual decrease to 400 m. Superimposed on this profile are three zones of anomalously low chlorinity. A similar situation is indicated on the salinity profile. If diffusion is an important process, then the initial increase in salinity produced by hydrate crystallization would be modified by diffusion into adjacent lower salinity zones. It is interesting to note that, according to our alternate interpretation, the maximum rate of "background" salinity and chlorinity increase embraces the three zones of anomalously low salinity/chlorinity values. This is consistent with diffusion of "high" salinity brine from hydrate zones into adjacent zones causing an increase in "background" salinity/chlorinity. The pore fluids collected from the three anomalous zones would then represent a mixture of pore fluid and 3 - 5% of dissociated hydrates. It should also be noted that the upper anomalous zone includes the depth (240 m) where hydrates were successfully recovered. Thus, it appears that these zones are associated with the presence of hydrates.

A carbonate alkalinity profile was also constructed for Site 533 pore fluid (Sheridan et al., 1983; Claypool and Threlkeld, 1983). The near-surface increase in alkalinity is due to sulfate reducing reactions which increase the pore fluid bicarbonate ion concentration, e.g.

in iron-free sediment:

$$2CH_2O + SO_4^{2-} \longrightarrow S^{2-} + 2CO_2 + SH_2O$$

$$S^{2-} + 2CO_2 + 2H_2O \longrightarrow H_2S + 2HCO_3^-$$
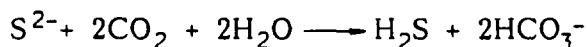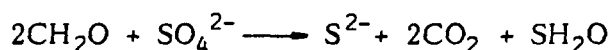
or in iron-bearing sediment:

$$6CH_2O + 3SO_4^{2-} + 2HFeO_2 \longrightarrow FeS + FeS_2 + 6HCO_3^- + 4H_2O$$

Below about 150 m, the alkalinity profile shows several major excursions. As was the case with salinity/chlorinity, the nature of the excursions depends upon the choosing of an appropriate "background". In Figure 19A, a low "background" profile would indicate four zones of anomalously high alkalinity which do not correlate with other chemical profiles, e.g. salinity/alkalinity. In Figure 19B, a high "background" would indicate three zones of anomalously low alkalinity which correspond almost exactly with the three zones of anomalously low salinity/chlorinity (Figure 18B). Such a correlation, if not fortuitous, suggests that there exists a relationship between anomalous alkalinity zones and hydrate formation. In this case, at least part of the alkalinity change may be a dilution effect due to the dissociation of hydrates. This is also suggested from the Ca^{2+} and Mg^{2+} profiles where obvious depletions at about 290 m could be due to a dilution effect (Figure 20).
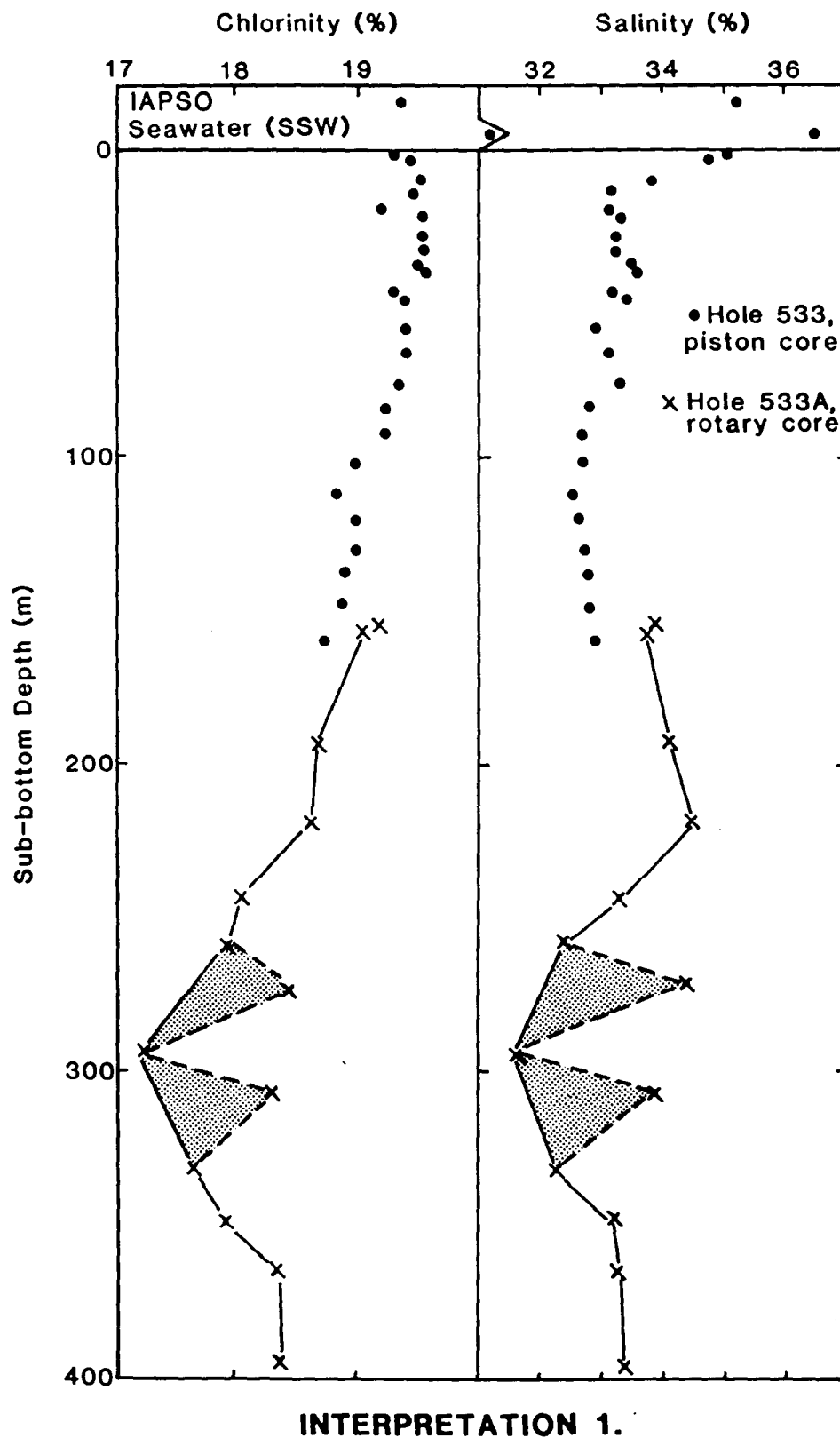
Figure 18A. PORE WATER CHLORINITY/SALINITY-DEPTH RELATIONS
AT DSDP SITE 533, BLAKE OUTER RIDGE

Data and Interpretation from DSDP

Figure 18B. PORE WATER CHLORINITY/SALINITY-DEPTH RELATIONS
AT DSDP SITE 533, BLAKE OUTER RIDGE

Data from DSDP Leg 76 Initial Report, reinterpreted
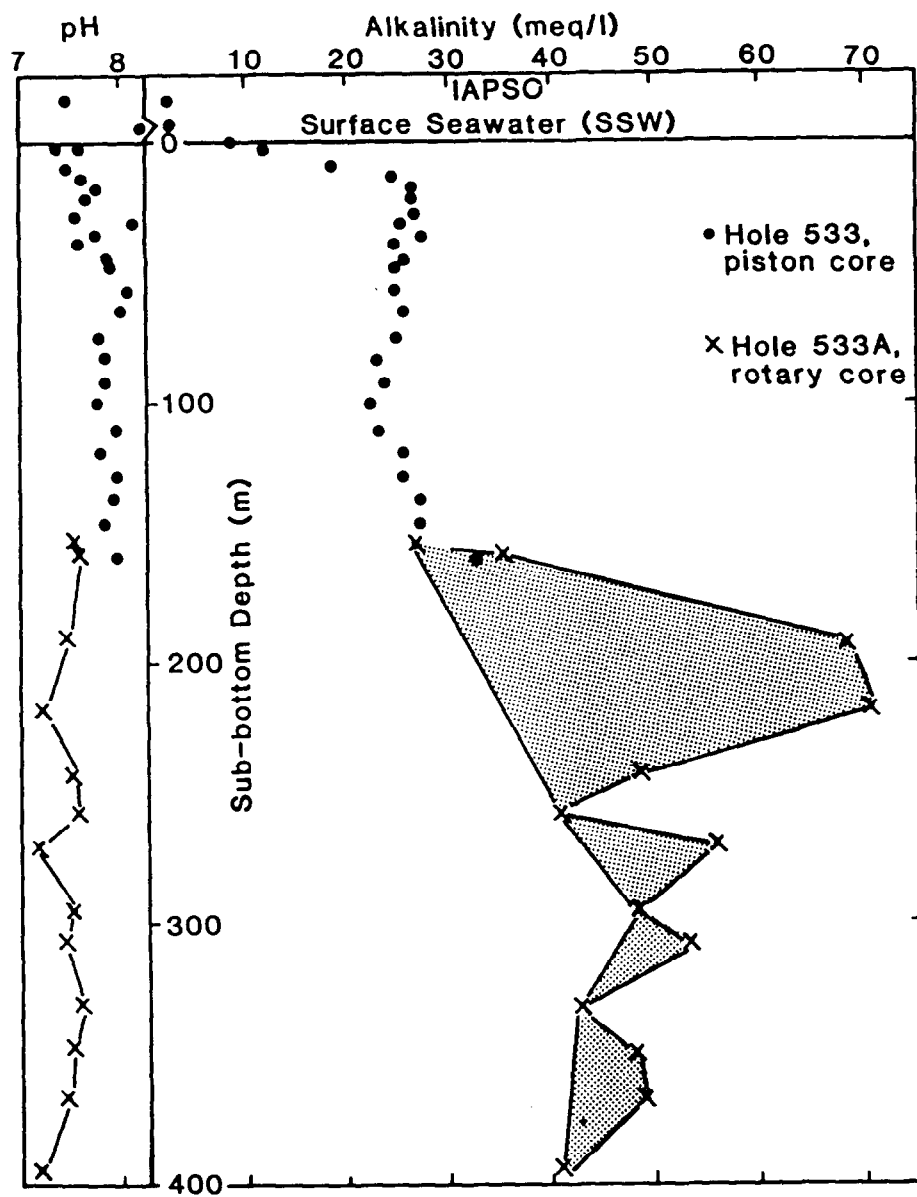
Figure 19A. PORE WATER ALKALINITY-DEPTH RELATIONS
AT DSDP SITE 533, BLAKE OUTER RIDGE

Data and interpretation of alkalinity profile from
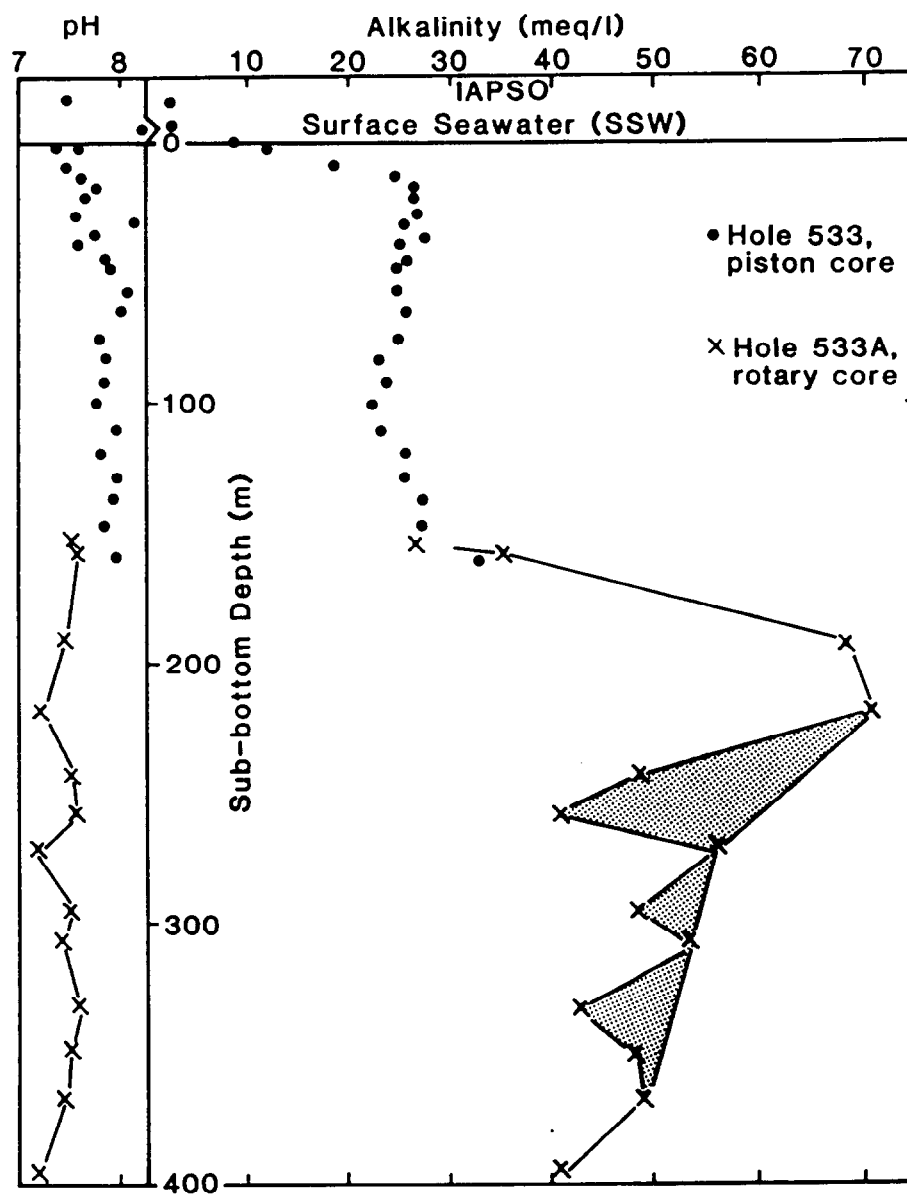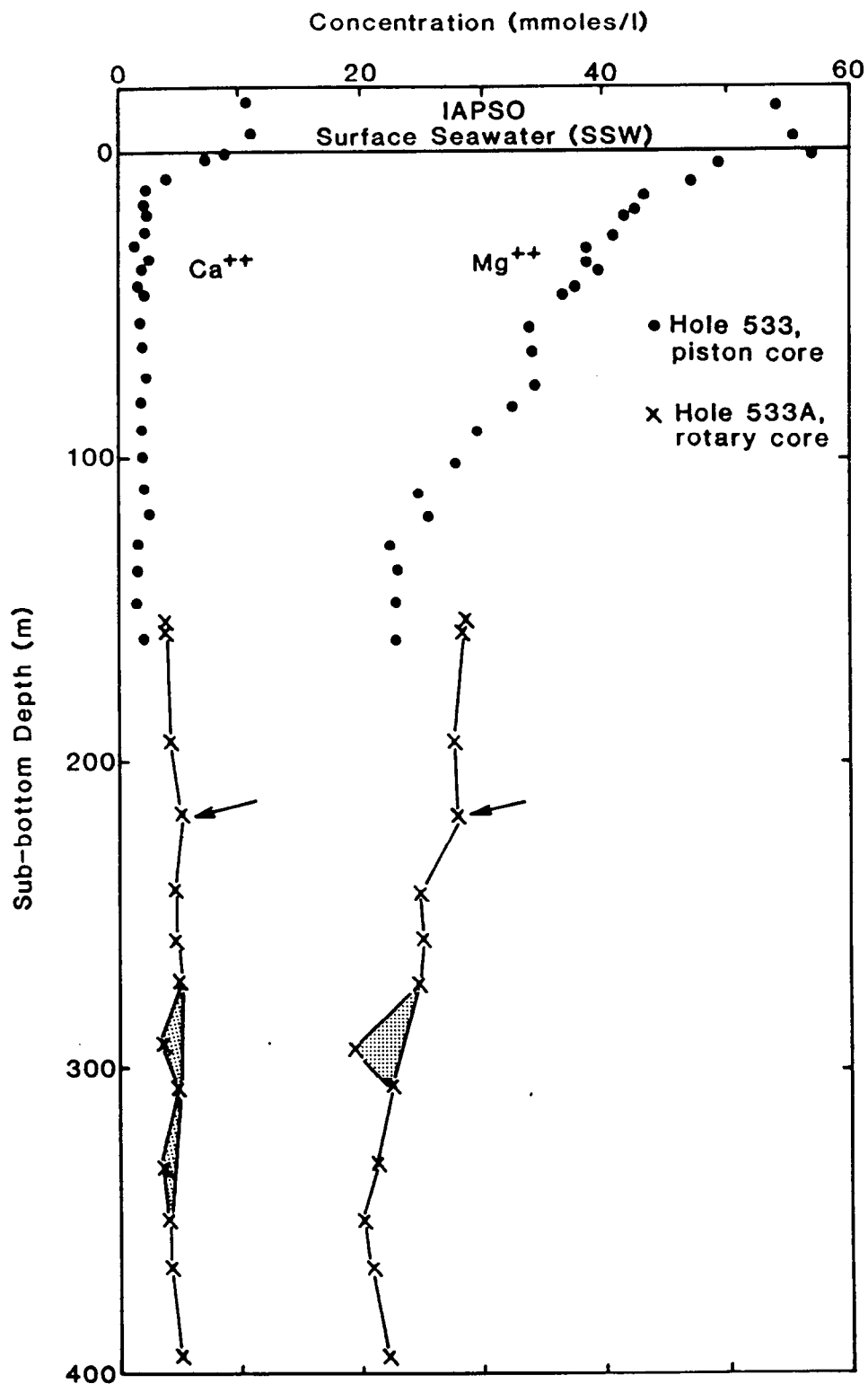DSDP Leg 76 Initial Report

INTERPRETATION 2.

**Figure 19B. PORE WATER ALKALINITY-DEPTH RELATIONS
AT DSDP SITE 533, BLAKE OUTER RIDGE**

Data from DSDP Leg 76 Initial Report, reinterpreted

Figure 20. CONCENTRATION OF Ca^{++} AND Mg^{++} IN
SEDIMENTS AT DSDP SITE 533
BLAKE OUTER RIDGE

Data from DSDP Leg 76 Initial Report

The alkalinity excursions are superimposed on a profile which shows a dramatic increase between 150 - 180 m. In this general depth zone are also observed layers and concretions of diagenetic limestones, dolomite and siderite (Figure 21) which must reduce sediment permeability. Figure 21 also indicates that carbonates are present throughout the section from 0 - 400 m but are particularly abundant in the zone discussed above and at about 290 m. Figure 19 shows that variations in pH are common below 200 m and in places are as low as 7.2. Such conditions may promote the dissolution of dolomite and calcite and release CO_2, Ca^{2+} and Mg^{2+}. Note the small increases in Ca^{2+} and Mg^{2+} in Figure 20. Release of CO_2 would thus increase bicarbonate ion concentration and generally raise the level of alkalinity throughout this section, as observed. The overall shape of the alkalinity curve (Figure 19B, interpretation 2) suggests that, if the increased alkalinity is related to CO_2 release, the layers and concretions of carbonate may act as an impermeable barrier to ascending CO_2 and the alkalinity subsequently rises beneath this barrier. Claypool and Threlkeld (1983) have also noted that the unusually high alkalinity is due to non-steady state production of CO_2, i.e. CO_2 in excess of that microbially reduced to CH_4. They propose, however, that the source of CO_2 is from decarboxylation reactions involving fatty acids, based on carbon isotopic values of -25 per mil. This obviously precludes a large contribution from nonbiological CO_2 (0 to -10 per mil), but some may nonetheless be present.

Gas Hydrate Formation and Diagenesis

A continuing arguement centers around the relative contributions of inorganic diagenesis, i.e. cementation, and hydrate formation to the physical properties of sediment above the BSR. Lancelot and Ewing (1970) have demonstrated carbonate cementation in sediments above the BSR at DSDP Sites 102, 103 and 104. The observed zonation from shallow calcite + dolomite + pyrite to siderite + ankerite + Mg-montmorillonite + pyrite at depth is pH and Eh controlled. At shallow depth an Eh of about -0.2 and pH above 7.8 stabilizes the observed assemblage, while a constant Eh but change in pH to 7 - 7.8 promotes the precipitation of iron carbonates at depth. At DSDP Site 533, carbonates also have precipitated throughout much of the section above the BSR, in places forming macroscopic layers and concretions (Sheridan et al., 1983; Matsumoto, 1983). Excepting these latter deposits, the amount of carbonate cement throughout the section does not appear to be exceptional (Figure 21). It is interesting to note that the large variations in carbonate alkalinity are not accompanied by similar variations in fluid pH (Figure 19B), except that the decrease in alkalinity below 200 m is accompanied by a small, gradual decrease in pH. Probably the high degree of ion complexing that occurs in these brine solutions causes only minor variations in pH over a wide range of alkalinity.

An important topic to address is the effect that pore fluid compositional variations near the limit of hydrate stability will have on carbonate precipitation. Here we only address the question in a qualitative manner. It appears likely that within the stability field of hydrates, changes in fluid composition brought about by hydrate crystallization will be partly reversed by diffusion. Thus, changes in pH will be over a small range, and a small amount of carbonate may or may not precipitate. However, the destruction

FIGURE 21. Distribution of Carbonate Minerals at DSDP
Site 533 Blake Outer Ridge, is located in the pocket
at the end of the report.

of hydrates at their stability limit introduces a large volume of fresh water which will dilute saline fluids above by diffusion. The effect may be to dramatically reduce the alkalinity and, more importantly, reduce the degree of ion complexing. Under such conditions, the decreased alkalinity may have a more pronounced effect on pH and prevent the precipitation of carbonate minerals. Thus, it is not apparent that conditions at the hydrate base would be conducive to the large-scale precipitation of carbonate minerals, if the influx of fresh water from below is an important process.

However, the situation is somewhat different if a thick, basal hydrate zone is largely impermeable to both the influx of fresh water from below and the outflow of in situ pore fluids. If hydrate crystallization is sufficiently advanced that the associated brines have developed an extreme alkalinity, then precipitation of carbonates may be significantly enhanced. Thus in this scenario, the hydrate base is also the site of increased carbonate precipitation which may contribute to an increased acoustic velocity contrast.

The conclusion is reached that within the stability field of hydrates, carbonate precipitation is possible but, in the absence of reactions which grossly effect the pH, is not excessive. At the hydrate base, the permeability largely controls the presence or absence of carbonate. If the base is permeable to fresh water influx, carbonate precipitation is prevented because of the decreased pH. If the base is impermeable to fluid flow, carbonate precipitation may be enhanced.

PART III

DEPOSITIONAL ANALYSIS

The thermal history of the Blake - Bahama Outer Ridge can be deduced through an analysis of the depositional history and inferred heat flow history. The depositional history is obtained from known or inferred stratigraphy based upon well data, e.g. DSDP Site 533, and/or seismic stratigraphy (Bryan and Heirtzler, 1984). The basic methodology is described in Sclater and Christie (1980) and Guidish et al. (1985). Individual parameters and their temporal variation are described below. The overall purpose of the analysis is to evaluate the time-dependent temperature distribution through the sedimentary pile in the context of gas hydrate stability. The conclusion is drawn that the temperature pressure conditions for hydrate stability have existed since about 34 m.y. ago but earlier conditions were unfavorable to gas hydrate formation.

Burial History

The simplest form of burial history curve is shown in Figure 22 based upon the idealized stratigraphic section illustrated for DSDP Site 533. The figure is constructed by linearly interpolating between the known age of the surface layer and its present thickness, moving each layer to the surface, and repeating the process.

Correction for compaction results in the burial history curve of Figure 23, based upon the assumption that shales and muds are the dominant lithology throughout the stratigraphic column. The compaction correction uses the BASIC program "POROSITY" based upon algorithms in Sclater and Christie (1980).

In Figure 23, the lower curve represents the relative movements of basement and the sediment-water interface. In normal basinal systems in which deposition is assumed to be facilitated by subsidence, this curve represents basement subsidence. In the Blake - Bahama Outer Ridge area, the post-34 m.y. history involves an upward growth of the ridge relative to basement, consequently the curve is not strictly a subsidence curve but represents burial of sediment relative to the sediment-water interface.
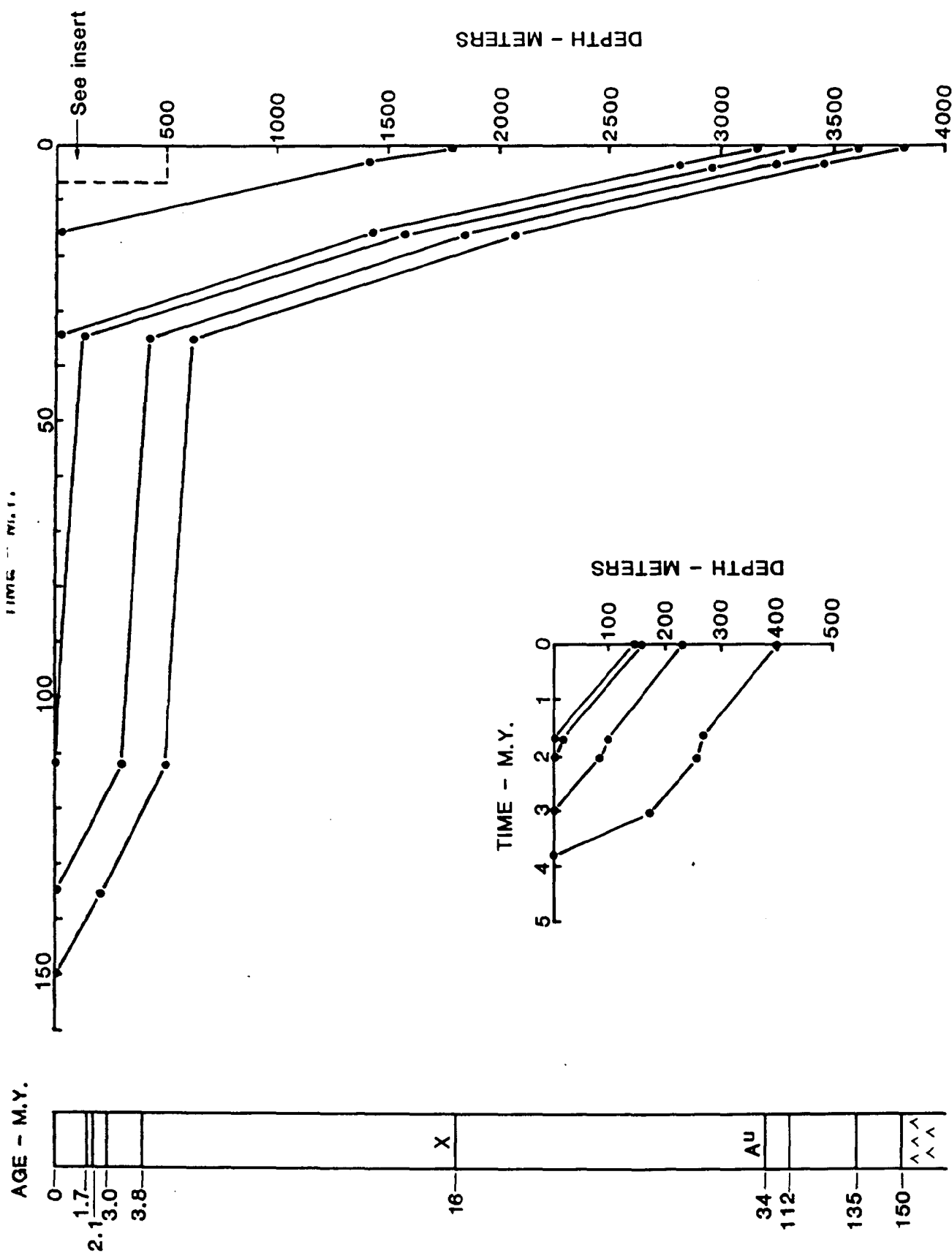
Figure 22. BURIAL HISTORY PLOT FOR DSDP SITE 533 TO OCEANIC BASEMENT, BLAKE OUTER RIDGE

Not corrected for compaction. The Pliocene – Pleistocene history is shown inset. Stratigraphic column (left) from which the curves were constructed is based on core data from DSDP Leg 76 Initial Report a   om   mic   tigr   da   Br)   nd   zler '   84)

- 76 -
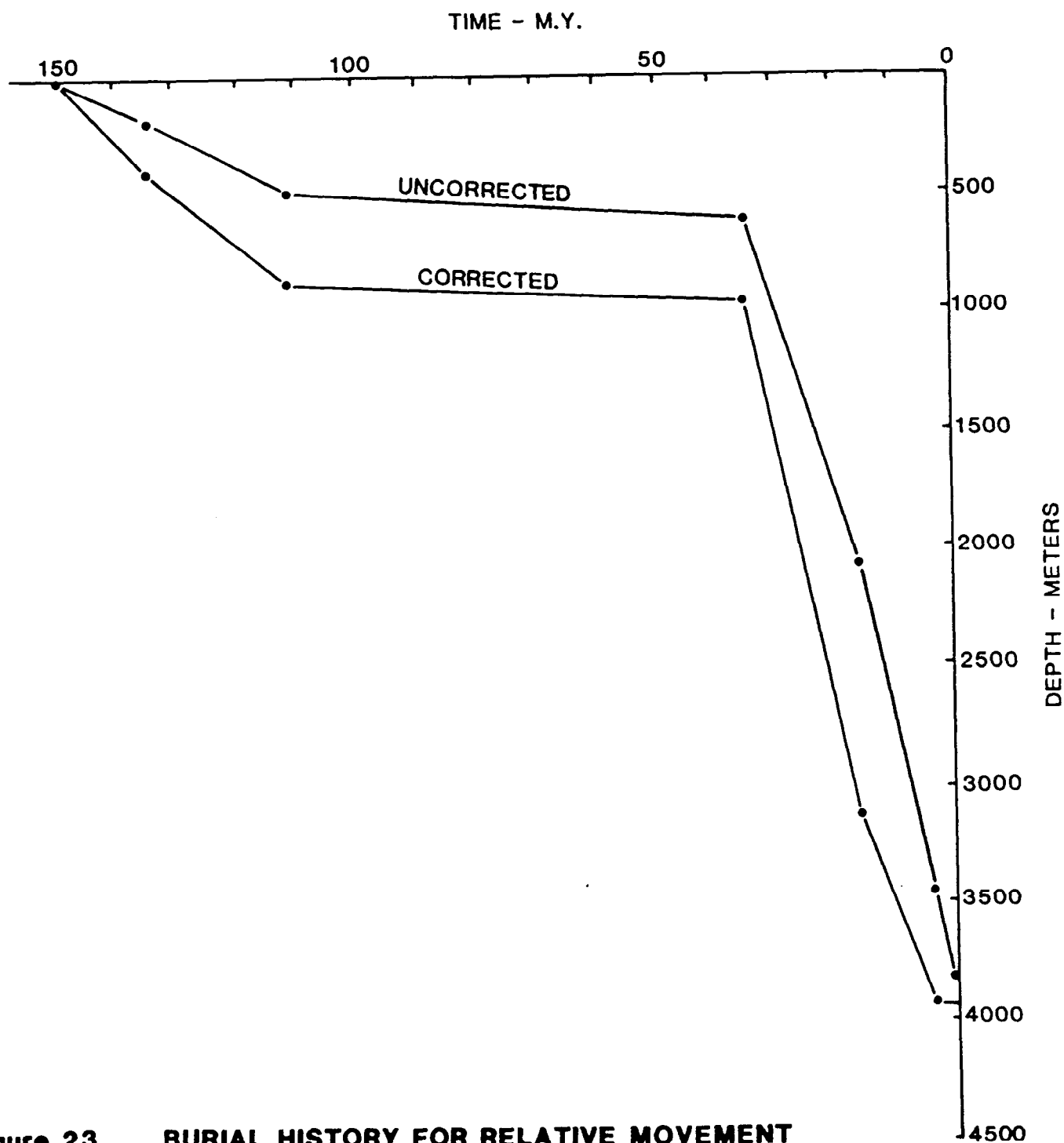
Figure 23. BURIAL HISTORY FOR RELATIVE MOVEMENT
OF BASEMENT (OCEANIC CRUST) AND
SEDIMENT-WATER INTERFACE AT DSDP SITE 533
BLAKE OUTER RIDGE

The uncorrected curve is from Figure 22. Lower curve has been corrected
for compaction using algorithm in Sclater and Christie (1980).

Water Depth

Figure 23 is uncorrected for water depth, i.e. is not referenced to sea level, because we have no independent measure of water depth throughout the section. At Site 533 the present water depth is about 3,800 m and presumably was deeper at earlier stages of ridge growth.

The Blake - Bahama Outer Ridge is floored partly by oceanic crust to the east and transitional continental crust to the west. The initial subsidence during Mesozoic rifting may therefore have been as small as 500 m to the west and as large as 2,500 m in the east. Note also that the form of the burial curve between 150 m.y. and 34 m.y. is that expected for basement undergoing thermal subsidence. The limited thickness of Mesozoic sediments also suggests that at the earliest stages of rifting, sediment loading was not the dominant contribution to subsidence.

Present Thermal Gradient

Only one temperature profile is available for this region, measured at DSDP Site 533. A gradient of 5.1°C/100 m is observed at 150 m, and 3.6°C/100 m to 400 m depth. The high near-surface value is probably a transient effect of surface erosion coupled with low thermal conductivity in near-surface sediments. The latter may be a close approach to the steady-state gradient, but the changing thermal conductivity of the sediments with depth suggests the thermal gradient will decrease with depth in the section.

Surface Temperature

The temperature at the sediment-water interface controls the temperature distribution in the sediments but not the thermal gradient. Bottom water temperature is a function of depth and therefore will vary over the Blake - Bahama Outer Ridge (Figure 15). At DSDP Site 533, the bottom water temperature is 2.4°C, and the minimum possible temperature at greater depths is assumed to be 2.15°C (Tucholke et al., 1977). This latter value is used in the thermal calculations for the ridge growth as a function of time, excepting the recent sedimentation, where the 2.4°C value is used. Temperatures approaching 0°C may have been present during periods of Pleistocene glaciation.

Lithologic Variation

It is assumed that the uniform muds and clays observed at the DSDP sites are the dominant lithologies throughout the post-basement depositional period, based upon the hemipelagic setting. Potential sandy units in the form of deep-sea fans may be present (Bryan and Heirtzler, 1984) but are not considered here as an important lithology.

Heat Flow

The measured thermal gradient and thermal conductivity of sediment at DSDP Site 533 imply a present thermal gradient of 1.1 heat flow units (HFU). This is consistent with the age of the basement and its assumed thermal evolution (Sclater and Christie, 1981). The variation in heat flow as a function of time is assumed to be an exponential function with a maximum value of 2.5 HFU at the time of rifting. This value may have been as high as 3 HFU.

Thermal Calculations

The steady-state thermal history can be deduced from the equation:

$$T_1 = T_0 + J + D/K$$

where T_1, T_0 = temperature at base and top of formation, respectively

K = thermal conductivity
J = heat flow
D = formation thickness

For a formation at the surface, T_0 is the bottom water temperature.

The unsteady (transient)-state gradients are determined from equations shown in Figure 24. Figure 25 shows the choices of initial thermal conditions used in the analysis.

Sedimentation Rates

The sedimentation rates were taken from DSDP Site 533 data or calculated from seismic stratigraphic data as shown in Table 6:

HEAT FLOW

$\longleftarrow \Delta x \longrightarrow$
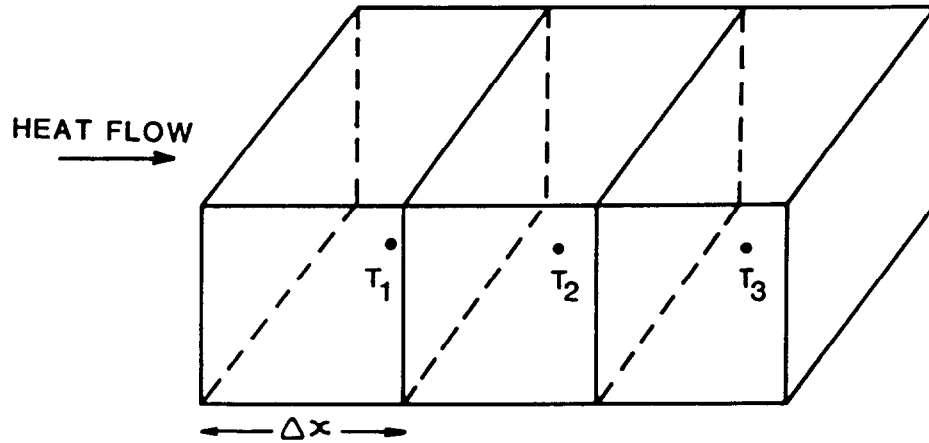
CONDITIONS: 1. UNIDIRECTIONAL HEAT FLOW
2. UNIFORM THERMAL DIFFUSIVITY

BASIC EQUATION:

$$T_2 = \frac{T_1 + T_3 + (M-2)T_2}{M}$$

$$M = \frac{(\Delta x)^2}{\alpha \Delta t}$$

WHERE: Δx = SIZE OF INDIVIDUAL CELLS
α = THERMAL DIFFUSIVITY
Δt = TIME STEP
T_1, T_2, T_3 = TEMPERATURES IN ADJACENT CELLS
T_2 = TEMPERATURE IN T_2 AFTER TIME Δt

BOUNDARY CONDITIONS: 1. INITIAL TEMPERATURE PROFILE
2. STEADY STATE TEMPERATURE PROFILE
3. SURFACE TEMPERATURE

Figure 24. PARAMETERS FOR UNSTEADY-STATE HEAT CONDUCTION SHOWN IN FIGURE 25
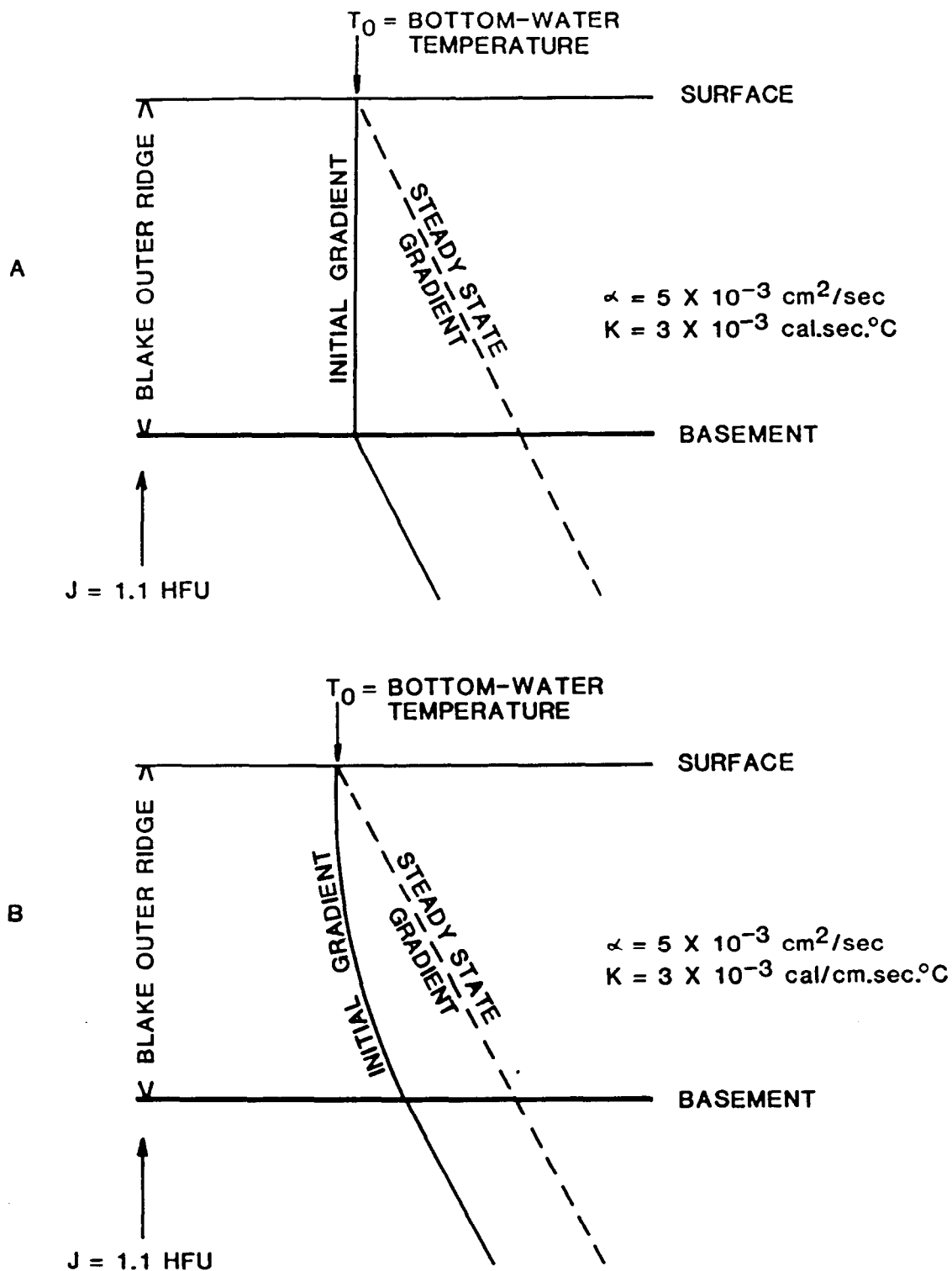
Figure 25. **INITIAL CONDITIONS EXAMINED IN THERMAL ANALYSIS BLAKE OUTER RIDGE**

Thermal analyses are for periods of high deposition rate: K is thermal conductivity, ⋞is thermal diffusivity. The heat flow at times of high deposition is assumed to be 1.1HFU

TABLE 6.

SEDIMENTATION RATES FOR DSDP SITE 533

Age m.y.	Sedimentation Rate m/m.y.
0 - 1.7	85
1.7 - 2.1	10
2.1 - 3.0	83
3.0 - 3.8	210
3.8 - 16*	114
16 - 34**	77
34 - 112^X	1.3
112 - 135*x	13
135 - 150+	13

* reflector X; ** A^u unconformity; ^{X} reflector J3;
*$_x$ reflector J2; + oceanic basement

The sedimentation rate has an effect on the thermal gradient. For rates less than about 100 m/m.y., the steady-state gradient is achieved at a rate faster than or comparable to the sedimentation rate. For higher sedimentation rates the thermal gradient is initially depressed and a series of transient gradients are produced. Note that the highest sedimentation rates are between 3.0 - 16 m.y. The resolution between 3.5 m.y. and 16 m.y. is poor, being based on seismic stratigraphy. Thus, there may exist within the latter time span periods of sedimentation greater than 150 - 200 m/m.y.

Table 6 indicates that the highest sedimentation rate at Site 533 occurred between 3.8 - 3.0 m.y. During this period the thermal gradient is initially depressed. Use of the basic equation in Figure 24 indicates that this transient gradient existed for less than 1 m.y., even using the extreme model in Figure 25A. Thus, we conclude that during the time-integrated history of the Blake Bahama Outer Ridge these transient events have a small effect on the steady-state conditions. Nonetheless, the depression of the geothermal gradient between 3.8 - 3.0 m.y., and possibly a smaller depression between 16 - 3.8 m.y., could have resulted in a hydrate zone thickness greater than currently observed. Gradual reestablishment of the steady-state gradient would have resulted in a reequilibration of the lower gas hydrate boundary through the dissociation of hydrates. Consequently, this time period would have seen the maximum liberation of a free gas phase.

If we examine the extreme model shown in Figure 25A for the time period from 3.8 - 3.6 m.y. and assume that hydrate formation rate is faster or comparable to the rate of temperature change in the sediment pile, then it is possible to chart the change in thickness of the hydrate zone as the temperature changes from the initial unsteady gradient to the final steady-state gradient. We also assume that prior to 3.8 m.y. the steady-state gradient was similar to the present-day value, i.e. 3.6°C/100 m. Under these conditions the hydrate zone would be thickest at the time of maximum temperature depression. Using the extreme profile of Figure 25A results in a zone thickness approximately 170 m thicker than observed at present. If the zone thickness decreased to the present thickness as the thermal gradient increased then 170 m of hydrates would dissociate.
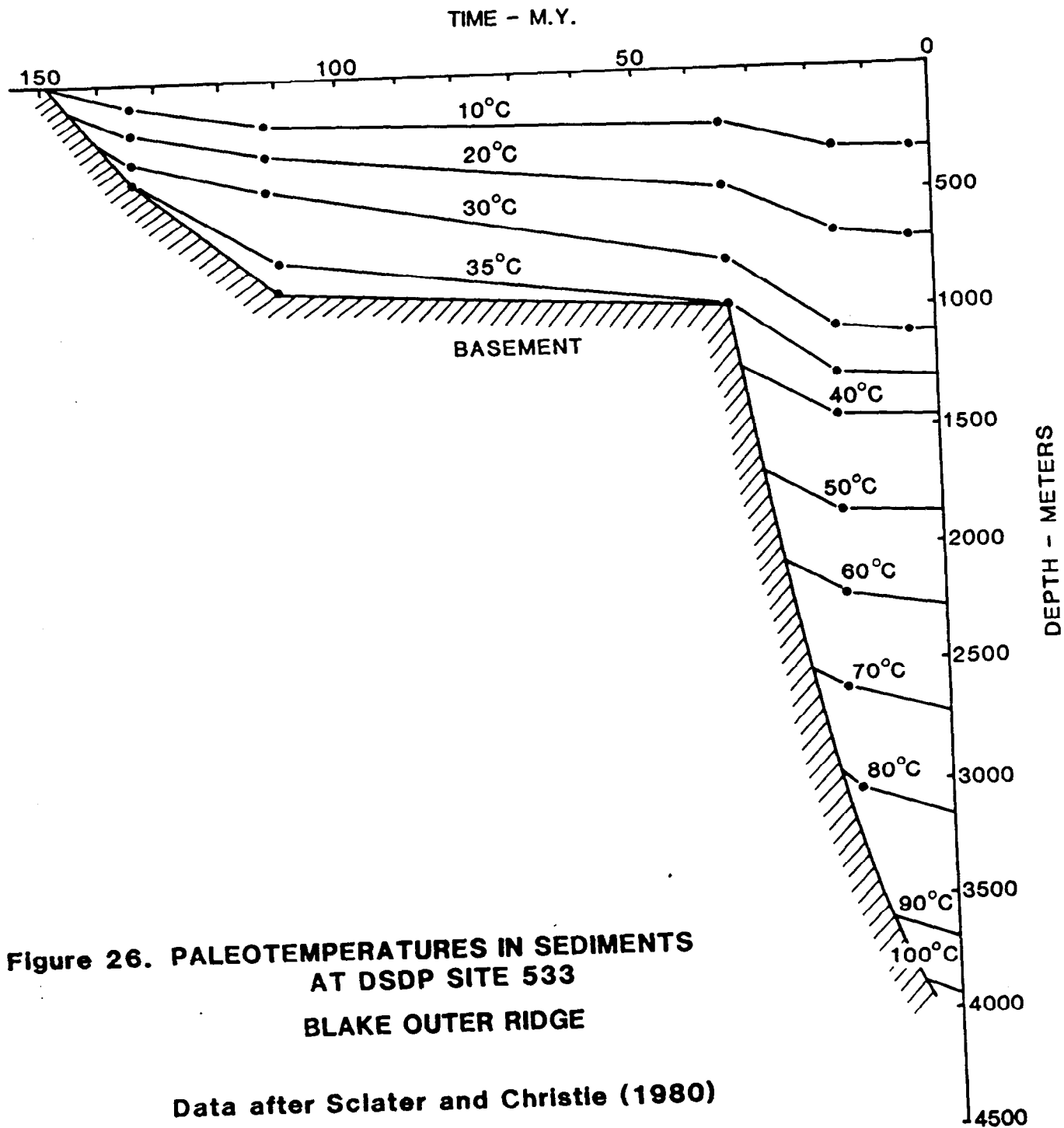
Thermal History

Paleotemperatures during the history of the Blake - Bahama Outer Ridge and sediments beneath the A^u unconformity are shown in Figure 26. At about 150 m.y. the continental margin basement was assumed to be at sea level and subsequently sank due to cooling. At this time, sediments began to accumulate at the margin. For the first several million years the sediment temperatures would have been high due to the high thermal gradients associated with the early rifting stage. It appears that between 150 m.y. and 34 m.y. the margin subsidence followed the exponential curve associated with cooling. By 34 m.y. approximately 1,000 m of sediment had accumulated in the vicinity of Site 533. Assuming that the heat flow perturbation had a time constant of 70 m.y. then by 80 m.y. the present steady-state heat flow gradient would have been established. Thus, barring effects of transient gradients discussed below, the potential existed for hydrate zones of present-day thickness to develop after 80 m.y., if the source of gas was biogenic.

At 34 m.y. the Blake - Bahama Outer Ridge was initiated as indicated by the steepening of the basement curve in Figure 26. As sediment accumulated, the temperature at any given depth above basement increased, and the potential for thermogenic hydrocarbon generation also increased. The temperature range for oil generation is generally assumed to be 60°C - 130°C. The lower value was attained at basement depths at about 28 m.y. and sediments deeper than approximately 2,200 m have had oil generative capability since that time. At present, all sediments below 2,200 m lie within the "oil window" and could be actively producing hydrocarbons from appropriate organic-rich lithologies.

The possibility also exists for the thermal generation of "early" gas and oil below 60°C, although the temperature range over which this maturation process occurs is poorly understood. Assuming this process began at 50°C then "early" gas could have been produced from approximately 31 m.y. to the present.

The formation of hydrates at the Blake - Bahama Outer Ridge appears to be the result of biogenic gas production, based on stable isotope studies, and does not involve a component of thermal gas. Nonetheless, we have demonstrated that the lower sedimentary sections do have the capability for thermal gas production which may migrate upwards and be trapped beneath a hydrate seal.

TIME – M.Y.

DEPTH – METERS

Figure 26. PALEOTEMPERATURES IN SEDIMENTS
AT DSDP SITE 533
BLAKE OUTER RIDGE

Data after Sclater and Christie (1980)

DISCUSSION

The geological history of the Blake - Bahama Outer Ridge has been described within the framework of the tectonic evolution of the continental margin. Prior to about 34 m.y. the sedimentation was normal with a relatively low rate of deposition on a slowly subsiding continental slope and rise. The A^u unconformity represents the approximate configuration of the rise and slope at early-middle Oligocene. The Blake Outer Ridge was built upon the A^u unconformity from about 34 m.y. to present during a period of anomalously high deposition. The configuration of the Blake - Bahama Outer Ridge can be modeled by assuming that deposition resulted through interaction of the northerly flowing Florida current and the southerly flowing western boundary undercurrent. Consequently, much of the sediment at the Blake - Bahama Outer Ridge was remobilized from the Blake Plateau. Once the ridge topography was developed it was further modified by the contouring effect of the western boundary undercurrent.

The presence of gas hydrates at the Blake Outer Ridge has been demonstrated through the recovery of hydrate-bearing sediment at DSDP Site 533 and indirectly through the recovery of anomalously gassy sediment cores. The areal extent of the hydrate zone can be mapped through the recognition of an acoustic bottom simulating reflector (BSR) on seismic sections. The BSR is assumed to be a reflection from the gas - gas hydrate contact at the base of the hydrate zone. Various classes of BSRs are discussed within the framework of hydrate formation in a dynamic depositional setting.

The chemical parameters that determine the stability of gas hydrates are reviewed and discussed within a geological context. The availability of methane at the Blake - Bahama Outer Ridge is determined by microbial activity and the preservation of sufficient organic matter to support such activity. Phase relations in the methane hydrate system are discussed in terms of open and closed systems which may be water-dominated or gas-dominated. The nucleation and growth of hydrates requires an unknown degree of supersaturation of the fluid phase with gas, which might be achieved during bubble formation. Hydrate crystallization is also facilitated by the presence of structured water at clay interfaces.

At the limit of gas hydrate stability, destruction of hydrates releases excess gas which may ascend and be reincorporated into hydrates within the stability field. Scenarios are discussed whereby "stranded" hydrate zones may develop as a result of a gas-dominated reservoir beneath the hydrate zone.

Examination of pore fluid chemistry at DSDP Site 533 suggests that anomalous zones of chlorinity, salinity and alkalinity are correlated, and possibly related to the presence of gas hydrates. The possibility that diagenesis, resulting in carbonate cement, may proceed in the hydrate zone is discussed, especially with reference to the zone close to the limit of hydrate stability.

CONCLUSIONS

1. The Blake - Bahama Outer Ridge developed because of an unusually high rate of deposition for the slope and rise environment. The sediment sources were the Blake Plateau and submarine margin areas north of the Blake Outer Ridge. Unusual deposition resulted from the interaction of the Gulf Stream and western boundary under-current.

2. The clastic flux, as computed for DSDP Sites 102, 103, 104, and 533 varies from 2 to 29 mg/cm^2/yr depending upon sediment age and location. The clastic fluxes at Sites 102 and 103 are almost identical, increasing from lower Miocene to Holocene. At Site 104 the opposite is true, with the higher fluxes recorded in the Miocene section. At Site 533 the Pliocene clastic flux is almost twice as high as calculated for the other sites, and the Pleistocene to Holocene flux is comparable to that observed at Sites 102 and 103 but significantly higher than observed at Site 104. The variations in clastic flux indicate a complex depositional pattern from the current system flowing around the outer ridge.

3. The organic matter flux is positively correlated with clastic flux at Sites 102, 103, 104 and 533, suggesting a relatively oxic depositional environment. Comparison with TOC measurements from similar environments indicates that TOC values in excess of 1 - 1.5% are unlikely to be found in this region. At Site 103 the fluxes are negatively correlated but the organic matter flux is very low (<0.1 mg/cm^2/yr). This correlation is unlikely to be due to simple sediment dilution in a strongly anoxic environment but may be caused by a very low flux of organic matter during deposition. The source of organic matter (and clastics?) at Site 103 appears to be different than for the other DSDP sites.

4. The organic matter flux at Site 102 is highest in the shallow Pleistocene to Holocene sediments (approximately 0.15 mg/cm^2/yr), which therefore are most prone to microbial methane production. The lower Miocene to Pliocene organic flux (0.06 mg/cm^2/yr) may be too low to produce sufficient methane for hydrate formation. Conversely, at Site 104, the highest organic fluxes are observed in the late to early Miocene sediments so that hydrates are more likely to be stabilized in this section. The late Miocene to Holocene sediments display a very low organic flux (0.02 mg/cm^2/yr), probably insufficient to stabilize hydrates. At Site 533 the organic fluxes are very high in the early Pliocene to late Pliocene section (0.14 - 0.38 mg/cm^2/yr) and would be expected to stabilize hydrates. The organic fluxes may be insufficient or marginally sufficient to stabilize hydrates.

5. At Site 103, the organic matter flux throughout the middle Miocene to Holocene section is consistently lower than that observed at the

other DSDP sites. This site may also be barren of hydrates, although this needs to be evaluated further. If the site is barren, then a lower limit for organic flux required to stabilize hydrates of approximately 0.1 mg/cm^2/yr is established.

6. The organic matter types at DSDP Site 533 include both terrestrial and marine components, based upon an interpretation of the carbon isotopic composition of extracted organic matter. The presence of significant terrestrial material may facilitate microbial methane production in suitably organic-rich sediments, as described above.

7. Calculations based on the methane requirements of gas hydrates with the maximum possible concentration of methane molecules, indicate that those sediments having the highest organic carbon content will have 5 - 10% of pore space occupied by hydrates; the remaining pore space will contain a brine solution. Alternatively, the hydrate component may be increased proportionately if the hydrate cages are not fully occupied by methane. Obviously, the lower the methane content of the hydrate, the less attractive becomes the hydrate as a potential resource.

8. The pore fluid has to become supersaturated with methane or other hydrate-forming gases in order to promote hydrate nucleation. The hydrate system also has to pass through a labile (unstable) stage in order to attain a stable equilibrium crystal growth stage. This can be achieved through an increase in temperature with burial. Although saturation of the pore fluid with methane is a minimum requirement for hydrate formation, it is also necessary to have available an excess volume of methane for incorporation into the hydrate cages.

9. Hydrate crystallization is promoted by the presence of "structured" versus "bulk" pore water. This ratio increases with burial depth in argillaceous sediments. Together with the increased potential for hydrate seed crystals with burial depth, this suggests that the proportion of hydrates in the pore space should increase with depth. Hydrate nucleation is promoted by large pore voids and throats. Therefore, hydrate growth may be initiated in coarser sediment intercalations and progress into finer lithologies.

10. The requirement for fluid supersaturation prior to hydrate formation is optimized near the lower hydrate boundary where an underlying zone of gas is available independent of microbial gas production. The critical factor here is the sediment permeability to upward gas migration into the hydrate zone.

11. Class 3 BSRs appear to be associated with areas of surface erosion. Under these conditions a transient thermal gradient is developed and results in the downward movement of the lower hydrate boundary. The diffuse character of the BSR in Class 3 reflections is considered to be due to the lack of an underlying free gas zone but does not

imply the absence of a hydrate zone. The vertical movement of the hydrate zone may result in "stranded" regions of hydrated-enriched sediment within the newly developed stability zone. This may be one way to develop nodular and massive hydrate textures.

12. The phase equilibrium relations for simple hydrate systems indicate that within the hydrate zone, the crystallization of hydrates can proceed under isothermal-isobaric conditions with a gradual increase in pore fluid salinity. If conditions were optimal for continuous hydrate growth, i.e. a sufficient reservoir of methane, then hydrate growth may be accompanied by the crystallization of halide minerals, e.g. NaCl, at high salinities. At the lower boundary of hydrate stability, hydrates cannot grow unconstrained because of the limits to pore fluid chemistry imposed by the divariant equilibrium. Hydrates can only continue to grow in the lower zone if the pore fluid composition is maintained invariant. This implies diffusion of ions through the fluid or flushing of fluids through the system.

13. The bottom water temperature over the Blake - Bahama Outer Ridge is sufficiently low to stabilize hydrates within the shallow sediments. Over those areas where BSRs have been located or hydrates recovered, the bottom water temperature is lower than 5.5°C, decreasing to about 2°C at 5,000 m water depth. Extrapolation of the bottom water/temperature depth curve for the western Atlantic Ocean suggests that the limits to hydrate stability would be at approximately 550 m water depth at a temperature of 5.5°C.

14. The thermal gradient at the Blake Outer Ridge is estimated to be 3.6°C/100 m based upon DSDP Site 533 measurements. The higher thermal gradient of 5°C/100 m measured at 150 m sediment depth is considered to be a transient gradient possibly related to local areas of surface sediment erosion. This thermal gradient implies a potential hydrate zone thickness of approximately 400 m.

15. Class 1 BSRs occupy an area of approximately 31,000 km^2 beneath the Blake - Bahama Outer Ridge. Class 2 and 3 reflectors occupy a further 22,000 km^2. If the sediment contained 100% hydrates, i.e. all pore space filled with hydrates, then 53,000 km^2 would contain the following gas volumes (in wellhead units; thicknesses measured upwards from a hydrate base at 400 m sediment depth; porosity 40%):

400 m	: 66 TCF
350 m	: 64 TCF
300 m	: 60 TCF
250 m	: 55 TCF
200 m	: 48 TCF
150 m	: 38 TCF
100 m	: 27 TCF
50 m	: 14 TCF

16. The idea that the distribution of the BSR may be due to favorable geometric relations between the hydrate base and underlying bedding planes continues to warrant consideration if the underlying lithologies are more permeable than normal mudstones and shales. For shales it is assumed that the dominant direction of gas migration will be vertical irrespective of the inclination of bedding planes. The movement of gas into and through the hydrate zone will also be dominated by a vertical component.

17. The pore fluid chemistry at DSDP Site 533 has been reinterpreted to provide a consistent relationship between chlorinity, salinity, alkalinity, pH, and cation content. Three zones of anomalously low salinity and chlorinity have been identified, one of which corresponds to the depth at which in situ hydrates were recovered. The low salinities are considered to be a dilution effect on residual pore fluid due to mixing with released fresh water accompanying hydrate dissociation during pore fluid sampling. The "background" profile of salinity and chlorinity is consistent with both upward and downward diffusion of saline fluid produced during hydrate formation.

18. At the DSDP sites, the section is weakly to moderately cemented with carbonate minerals, excepting local horizons where extensive carbonate cementation corresponds to dramatic increases in pore fluid alkalinity. Permeability at the lower boundary of chemically distinct, i.e. fresher, pore fluid determines the stability of carbonate minerals in the lower hydrate zone.

19. A thermal analysis suggests that hydrates could have been stabilized after about 34 m.y. the (A^u unconformity) until the present to at least the present thickness. The thickest hydrate zones would have existed during periods of sedimentation greater than 100 m/m.y. because of depressed, but transient, thermal gradients. From 34 m.y. to present, the stabilization then destruction of hydrates would have generated large volumes of gas, parts of which may still remain trapped if suitable lithologic and structural conditions permit. The pre-Oligocene section is thin, and heat flow may have been too high during deposition to stabilize a substantial thickness of hydrates, especially in the absence of sufficient organic material.

REFERENCES

Anderson, D.M., and Low, P.F., 1958, The density of water adsorbed by lithium, sodium, and potassium bentonite: Soil Sci. Soc. Am. Proc., v. 22, p. 99.

Anderson, R.C., Wise R.A., and Dillon, W.P., 1981, Seismic investigations of gas hydrate reflectors, Blake Outer Ridge area off southeastern United States (abs.): Am. Assoc. Petroleum Geologists Bull., v. 65, p. 890.

Andrews, J.E., 1967, Blake Outer Ridge: Development by gravity tectonics: Science, v. 156, p. 642.

Bally, A.W., 1981, Atlantic-type margins, in Bally, A.W., compiler, Geology of passive continental margins: history, structure and sedimentologic record (with special emphasis on the Atlantic margin): Am. Assoc. Petroleum Geologists, Education Course Note Series 19, p. 1-1.

Barefoot, R.R., and van Elsberg, J.N., 1975, The role of adsorbed or structured water in the diagenesis of the Tertiary sediments in the Mackenzie Delta; a preliminary report: Canada Geol. Survey Paper 75-1C, 303 p.

Barrett, J.R., 1965, Subsurface currents off Cape Hatteras: Deep Sea Research, v. 12, p. 173.

Barrett, D.L., and Keen,C.E., 1976, Mesozoic magnetic lineations, the magnetic quiet zone, and sea-floor spreading in the North Atlantic: Jour. Geophys. Research, v. 81, p. 4875.

Benson, W.E., Sheridan, R.E., and others, 1978, Sites 389 and 390: North rim of Blake nose, in Initial reports of Deep Sea Drilling Project: Washington, U.S. Govt. Printing Office, v. 44, p. 69.

Berecz, E., and Balla-Achs, M., 1983, Gas hydrates: Elsevier Amsterdam – Budapest, 343 p.

Brock, J.M., Barnard, L.A., Weisenberg, D.A., Kennicutt, M.C. II, and Kvenvolden, K.A., 1983, Molecular and isotopic compositions of hydrocarbons at Site 533, Deep Sea Drilling Project, Leg 76, in Initial reports of the Deep Sea Drilling Project, Norfolk, Virginia to Fort Lauderdale, Florida: Washington, U.S. Govt. Printing Office, v. 76, p. 377.

Boyce, R.E., 1972, Carbon and carbonate analyses, Leg 11, in Initial reports of Deep Sea Drilling Project: Washington, U.S. Govt. Printing Office, v. 11, p. 1059.

Bryan, G.M., 1970a, Hydrodynamic model of the Blake Outer Ridge: Jour. Geophys. Research, v. 75, p. 4530.

Bryan, G.M., 1970b, Hydrodynamic model of the Blake Outer Ridge: Jour. Geophys. Research, v. 75, p. 5430.

Bryan, G.M., 1974, In situ indications of gas hydrates, in Kaplan, I.R., ed., Natural Gases in Marine Sediments: New York, Plenum Press, p. 299.

Bryan, G.M., and Heirztler, J.R., 1984, Eastern North American continental margin and adjacent ocean floor, 28° to 36°N and 70° to 82°W: Ocean Margin Drilling Program, Regional Atlas Series, Marine Science International, Woods Hole, Massachusetts, Atlas 5.

Bryan, G.M., and Markl, R.G., 1966, Microtopography of the Blake – Bahama region: Lamont-Doherty Geol. Observatory, Technical Report 8.

Burst, J.F., 1976, Argillaceous sediment dewatering: Ann. Review of Earth and Planetary Sci., v. 4, p. 293.

Claypool, G.E., and Kaplan, I.R., 1974, The origin and distribution of methane in marine sediments, in I.R. Kaplan, ed., Natural Gases in Marine Sediments: Plenum, New York, p. 99.

Claypool, G.E., and Kvenvolden, K.A., 1983, Methane and other hydrocarbon gases in marine sediments: Ann. Review of Earth and Planetary Sci., v. 11, p. 299.

Claypool, G.E., Presley, B.J., and Kaplan, I.R., 1973, Gas analysis in sediment samples from Legs 10, 11, 13, 14, 15, 18 and 19, in Initial reports of the Deep Sea Drilling Project, Kodiak, Alaska to Yokohama, Japan: Washington, Govt. Printing Office, v. 19, p. 879.

Claypool, G.E., and Threlkeld, C.N., 1983, Anoxic diagenesis and methane diagenesis in sediments of the Blake Outer Ridge, DSDP Site 533, Leg 76, in Initial reports of the Deep Sea Drillling Project, Norfolk, Virginia to Fort Lauderdale, Florida: Washington, U.S. Govt. Printing Office, v. 76, p. 391.

Collett, T.S., 1984, Hydrate evaluation on the north slope of Alaska: Poster Sessions, U.S. Geol. Survey Petroleum Research Symposium, October 10 - 11, Golden, Colorado.

Culbertson, O.L., and McKetta, J.J., 1951, The solubility of methane in water at pressures to 10,000 psi: Am. Inst. Mining Engineers, Trans., v. 192., p. 223.

Davy, H., 1811, On some of the combinations of oxy-muriatic gas and oxygen and on the chemical relations of the principles to inflammable bodies: Royal Soc. of London Philosophical Trans., v. 101, p. 1.

Deaton, W.M., and Frost, E.M., 1937, Gas hydrates in natural gas pipelines: Oil and Gas Jour., v. 36, May 27, p. 75.

Deaton, W.M., and Frost, E.M., 1948, Gas hydrates and their relation to the operation of natural gas pipelines: U.S. Bureau Mines Monograph, no. 8, 101 p.

Dillon, W.P., Grow, J.A., and Pauli, C.K., 1980, Unconventional gas hydrate seals may trap gas off southeast U.S.: Oil and Gas Jour., v. 78, no. 1, p. 124.

Dillon, W.P., and Paull, C.K., 1983, Marine gas hydrates - II. Geophysical evidence, in J.L. Cox, ed., Natural Gas Hydrates: Properties, Occurrences, and Recovery: Boston, Butterworth Publ., p. 73.

Drake, C.L., Ewing, J.I., and Stockard, H., 1968, The continental margin of the eastern United States: Canadian Jour. Earth Sci., v. 5, p. 993.

Dillon, W.P., and Paull, C.K., 1983, Marine gas hydrates - II. Geophysical evidence, in Cox, J.L., ed., Natural Gas Hydrates: Properties, Occurrences and Recovery: Boston, Butterworth Publ., p. 128.

Dillon, W.P., Paull, C.K., Buffler, R.T., and Fail, J.P., 1979, Structure and development of the southeast Georgia Embayment and Northern Blake Plateau - a preliminary analysis, in Watkins, J.S., Montadert, L., and Dickerson, P.W., eds., Geological and geophysical investigations of continental margins: Am. Assoc. Petroleum Geologists Mem. 29, p. 27.

Ewing, M., and Ewing, J.I., 1964, Distribution of oceanic sediments, in Univ. Tokyo Geophys. Institute, Studies in Oceanography: Tokyo, p. 525.

Ewing, J.I., Ewing, M., and Leyden, R., 1966, Seismic-profiler survey of the Blake plateau: Am. Assoc. Petroleum Geologists Bull., v. 50, p. 1948.

Eittreim, S.L., Ewing, M., and Thorndike, E.M., 1969, Suspended matter along the continental margin of the North American Basin: Deep Sea Research, v. 16, p. 613.

Frost, E.M., and Deaton, W.M., 1946, Gas hydrate composition and equilibrium data: Oil and Gas Jour., v. 45, p. 170.

Galimov, E.M., and Kvenvolden, K.A., 1983, Concentration and carbon isotopic compositions of CH_4 and CO_2 in gases from sediments of the Blake Outer Ridge, Deep Sea Drilling Project, Leg 76, in Initial reports of the Deep Sea Drilling Project, Norfolk, Virginia to Fort Lauderdale, Florida: Washington, U.S. Govt. Printing Office, v. 76, p. 403.

Gradstein, F.M., and Sheridan, R.E., 1983, Site reports and underway data: Introduction, in Initial reports of the Deep Sea Drilling Project, Norfolk, Virginia to Fort Lauderdale, Florida: Washington, U.S. Govt. Printing Ofice, v. 76, p. 5.

Grow, J.A., 1981, The Atlantic margin of the United States, in Bally, A.W. compiler, Geology of passive continental margins: history structure and sedimentologic record (with special emphasis on the Atlantic margin): Am. Assoc. Petroleum Geologists, Education Course Note Series 19, p. 5-1.

Grow, J.A., Hutchinson, D.R., Klitgord, K.D., Dillon, W.P., and Schlee, J.S., 1983, Representative multichannel seismic profiles over the U.S. Atlantic margin, in Bally, A.W., ed., Seismic expression of structural styles - a picture and work atlas: Am. Assoc. Petroleum Geologists, Studies in Geology 15, v. 2, p. 2.3-1.

Grow, J.S., Mattick, R.E., and Schlee, J.J., 1979, Multichannel seismic depth section and interval velocities over Outer Continental Shelf and Upper Continental Slope between Cape Hatteras and Cape Cod, in Watkins, J.S., Montadert, L., and Dickerson, P.W., eds., Geological and geophysical investigations of continental margins: Am. Assoc. Petroleum Geologists Mem. 29, p. 65.

Grow, J.A., and Sheridan, R.E., 1981, Deep structure and evolution of the continental margin off the eastern United States: Internat. Geol. Cong., 26th Paris, France, 1980, Colloque C3, Geologie des marges continentales: Oceanologica Acta, no. SP, p. 11.

Grow, J.A., and Sheridan, R.E., 1982, Atlantic continental margin of the United States, in Palmer, A.R., ed., Regional geological synthesis: Geol. Soc. America, Decade of North American Geology Special Pub. 1, p. 14.

Guidish, T.M., Kendall, C.G.St.C., Lerche, I., Toth, D.J., and Yarzab, R.F., 1985, Basin evaluation using burial history calculations: a review: Am. Assoc. Petroleum Geologists Bull., v. 69, p. 92.

Hammerschmidt, E.G., 1934, Formation of gas hydrates in natural gas transmission lines: Industrial and Engineering Chemistry, v. 26, p. 851.

Hand, J.J., Katz, D.L., and Verma, V.K., 1974, Review of gas hydrates with implications for oceanic sediments, in Kaplan, I.R., ed., Natural Gases in Marine Sediments: New York, Plenum Press, p. 179.

Heezen, B.C., Hollister, C.D., and Raddiman, W.F., 1966a, Shaping of the continental rise by geostrophic contour currents: Science, v. 152, p. 502.

Heezen, B.C., Hollister, C.D., and Raddiman, W.F., 1966b, Shaping of the continental rise by deep geostrophic contour currents: Science, v. 152, p. 3721.

Hersey, J.G., Bunce, E.T., Wyrick, R.F., and Dietz, F.T., 1959, Geophysical investigation of the continental margin between Cape Henry, Virginia and Jacksonville, Florida: Geol. Soc. America Bull., v. 70, p. 437 - 466.

Hitchon, B., 1974, Occurrence of natural gas hydrates in sedimentary basins, in Kaplan, I.R., ed., Natural Gases in Marine Sediments: New York, Plenum Press, p. 195.

Holder, G.D., and Grigoriou, 1980, Hydrate dissociation pressures of (Methane + Ethane + Water): Existence of a locus of minimum pressures: Jour. Chem. Thermodyn., v. 12, p. 1093.

Hollister, C.D., Ewing, J.I, and others, 1972, Sites 102, 103, 104: Blake - Bahama Outer Ridge (Northern End), in Initial reports of Deep Sea Drilling Project, Miami, Florida to Hoboken, New Jersey: Washington, U.S. Govt. Printing Office, v. 11, p. 135.

Hutchison, D.R., Grow, J.A., Klitgord, K.D., and Swift, B.A., 1983, Deep structure and evolution of the Carolina Trough, in Watkins, J.S., and Drake, C.L., eds., Studies in continental marine geology: Am. Assoc. Petroleum Geologists Mem. 34, p. 129.

Jansa, L.F., Enos, P., Tucholke, B.E., Gradstein, F.M., and Sheridan, R.E., 1979, Mesozoic-Cenozoic sedimentary formations of the North American Basin, western North Atlantic, in Talwani, M., Hay, W., and Ryan, W.B.F., eds., Deep drilling results in the Atlantic Ocean: continental margins and paleoenvironment: Am. Geophys. Union, Maurice Ewing Series, v. 3, p. 1.

Judge, A., 1984, Natural gas hydrates in the MacKenzie Delta-Beaufort Sea areas of northern Canada: Am. Inst. Chem. Eng., Winter Nat. Meeting, Atlanta, Georgia.

Katz, D.L., Cornell, D., Kobayashi, R., Poettman, F.H., Vary, J.A., Elenbass, J.R., and Weinauy, C.F., 1959, Handbook of Natural Gas Engineering: New York, McGraw-Hill, 207 p.

Keen, M.J., 1969, Magnetic anomalies off the eastern seaboard of the United States - a possible edge effect: Nature, v. 222, p. 72.

Keen, C.E., 1983, Salt diapirs and thermal maturity: Scotian basin: Canadian Petroleum Geology Bull., v. 31, no. 2, p. 101.

Kent, K.M., 1979, Two-dimentional gravity model of the Southeast Georgia Embayment - Blake Plateau: M.S. Thesis, Univ. Delaware, 89 p.

Klitgord, K.D., and Behrendt, J.C., 1979, Basin structure of the U.S. Atlantic margin, in Watkins, J.S., Montadert, L., and Dickerson, P.W., eds., Geological and Geophysical Investigations of Continental Margins: Amer. Assoc. Petroleum Geologists Mem. 29, p. 85.

Klitgord, K.D., and Grow, J.A., 1980, Jurassic seismic stratigraphy and basement of the Western Atlantic magnetic quiet zone: Am. Assoc. Petroleum Geologists Bull., v. 64, p. 1658.

Kobayashi, R., and Katz, D.L., 1949, Methane hydrate at high pressure: Am. Inst. Mining Engineers, Petroleum Transactions, v. 186, p. 66.

Kuuskraa, V.A., Hummershaimb, E.C., Holder, G.D., Sloan, E.D., 1983, Handbook of Gas Hydrate Properties: U.S. Department of Energy, DOE/MC/19239-1546, 234 p.

Kvenvolden, K.A., 1984, Hydrates and deep source of gas: U.S. Geol. Survey Petroleum Resources Symposium, Golden, Colorado.

Kvenvolden, K.A., 1983, Marine gas hydrates - I: Geochemical evidence, in Cox, J.L., ed., Natural gas hydrates: properties, occurrence and recovery: Boston, Butterworth Publ., p. 63.

Kvenvolden, K.A., and Barnard, L.A., 1983a, Hydrates of natural gas in continental margins, in Watkins, J.S., and Drake, C.L., eds., Studies in continental margin geology: Am. Assoc. Petroleum Geologists Mem. 34, p. 631.

Kvenvolden, K.A., and Barnard, L.A., 1983b, Gas hydrates of the Blake Outer Ridge, Site 533, Initial reports of the Deep Sea Drilling Project, Norfolk, Virginia to Fort Lauderdale, Florida: Washington, U.S. Govt. Printing Office, v. 76, p. 353.

Kvenvolden, K.A., and McMenamin, M.A., 1980, Hydrates of natural gas: a review of their geological occurrences: U.S. Geol. Survey Circ. 825, 11 p.

Lancelot, Y., and Ewing, J.I., 1972, Correlation of natural gas zonation and carbonate diagenesis in Tertiary sediments from the northwest Atlantic, in Initial reports of Deep Sea Drilling Project, Miami, Florida to Hoboken, New Jersey: Washington, U.S. Govt. Printing Office, v. 11, p. 791.

Long, F.A., and McDevit, W.F., 1952, Activity coefficients of non-electrolyte solutes in aqueous salt solutions: Chem. Review, v. 51, p. 119.

Low, P.F., 1961, Physical chemistry of clay-water interactions: Adv. in Agron., v. 13, p. 269.

Makogon, Y.F., 1965, Hydrate formation in the gas-bearing beds under permafrost conditons, (in Russian): Gazovaia promyschlennost, No. 5, p. 14.

Makogon, Y.F., 1978, Hydrates of Natural Gas: (Trans. from Russian by W.J. Cieslewicz): Denver, Geoexplorers Associates, Inc., 178 p.

Manspeizer, W., 1981, Early Mesozoic basins of the Central Atlantic passive margins, in Bally, A.W., compiler, Geology of passive continental margins: history, structure and sedimentologic record (with special emphasis on the Atlantic margin): Am. Assoc. Petroleum Geologists, Education Course Note Series 19, p. 4-1.

Markl, R.G., Bryan, G.M., and Ewing, J.I., 1970, Structure of the Blake - Bahama Outer Ridge: Jour. Geophys. Research, v. 75, p. 4539.

Matsumoto, R., 1983, Mineralogy and geochemistry of carbonate diagenesis of the Pliocene and Pleistocene hemipelagic mud on the Blake Outer Ridge, Site 533, Leg 76, in Initial reports of the Deep Sea Drilling Project, Norfolk, Virginia to Fort Lauderdale, Florida: Washington, U.S. Govt. Printing Office, v. 76, p. 411.

McIver, R.D., 1974, Hydrocarbon gas (methane) in canned Deep Sea Drilling Project samples, in Kaplan, I.R., ed., Natural Gases in Marine Sediments: New York, Plenum Press, p. 63.

Miller, S.L., 1974, The nature and occurrence of clathrate hydrates, in Kaplan, I.R., ed., Natural gases in marine sediments: New York, Plenum Press, p. 151.

Paull, C.K., and Dillon, W.P., 1981, Appearance and distribution of the gas hydrate reflection in the Blake Ridge region, offshore southeastern U.S.: U.S. Geol. Surv. Misc. Field Studies Map MF-1252.

Paull, C.K., Popenoe, P., Dillon, W.P., and McCarthy, S.M., 1980, Geologic subcrop map of the Florida-Hatteras shelf and slope, and Inner Blake Plateau: U.S. Geol. Surv. Misc. Field Studies Map MF-1171.

Pratt, R.M., 1963, Bottom currents on the Blake Plateau: Deep Sea Research, v. 10, p. 245.

Pratt, R.M., and Heezen, B.C., 1964, Topgraphy of the Blake Plateau: Deep Sea Research, v. 11, p. 721.

Presley, B.J., and Kaplan, I.R., 1972, Interstitial water chemistry: Deep Sea Drilling Project, Leg 11, in Initial reports of the Deep Sea Drilling Project, Miami, Florida to Hoboken, New Jersey: Washington, U.S. Govt. Printing Office, v. 11, p. 1009.

Rashid, M.A., and Vilks, G., 1977, Environmental controls of methane production in Holocene basins in eastern Canada: Organic Geochem., v. 1, p. 53.

Rice, D.D., and Claypool, G.E., 1981, Generation, accumulation, and resource potential of biogenic gas: Am. Assoc. Petroleum Geologists Bull., v. 65, p. 5.

Roberts, O.L., Brownscombe, E.R., Howe, L.S., and Ramser, H., 1941, Phase diagrams of methane and ethane hydrates: The Petroleum Engineer (March).

Rona, P.A., and Clay, C.S., 1967, Stratigraphy and structure along a continuous seismic reflection profile from Cape Hatteras, North Carolina to the Bermuda Rise: Jour. Geophys. Research, v. 72, p. 2107.

Rowe, G.T., and Menzies, R.J., 1968, Deep currents off the coast of North Carolina: Deep Sea Research, v. 15, p. 711.

Sayles, F.L., Manheim, F.T., and Waterman, L.W., 1972, Interstitial water studies on small core samples, Leg 11, in Initial reports of Deep Sea Drilling Project, Miami, Florida to Hoboken, New Jersey: Washington, U.S. Govt. Printing Office, v. 11, p. 997.

Schlee, J.S., 1981, Seismic stratigrahy of the Baltimore Canyon Trough: Am. Assoc. Petroleum Geologicst Bull., v. 65, p. 26.

Schwarzer, T.F., 1966, A theoretical treatment of the non-freezable behavior of certain argillaceous dolomites: M.S. Thesis, Rennselaer Poly. Inst., Troy, N.Y.

Sclater, J.G., and Christie, P.A.F., 1980, Continental stretching: and explanation of the post mid-Cretaceous subsidence of the central North Sea basin: Jour. Geophys. Research, v. 85, p. 3711.

Sheridan, R.E., 1978a, Structure, stratigraphy, evolution, and petroleum potential of the Blake Plateau: 10th Ann. Offshore Technology Conf. Proc., v. 1, p. 363.

Sheridan, R.E., 1978b, Structure, stratigraphy, evolution, and petroleum potential of the Blake Plateau: 10th Ann. Offshore Technology Conf. Proc., v. 1, p. 391.

Sheridan, R.E., Gradstein, F.M., and others, 1982, Early history of the Atlantic Ocean and gas hydrates in the Blake Outer Ridge: results of the Deep Sea Drilling Project, Leg 76: Geol. Society America Bull., v. 93, no. 9, p. 876.

Sheridan, R.E., Gradstein, F.M., and others, 1983, Appendix 1: Carbon and carbonate analyses, Leg 76, in Initial reports of the Deep Sea Drilling Project, Norfolk, Virginia to Fort Lauderdale, Florida: Washington, U.S. Govt. Printing Office, v. 76, p. 945.

Sheridan, R.E., Grow, J.A., Behrendt, J.C., and Bayer, K.C., 1979, Seismic refraction study of the continental edge off the eastern United States: Tectonophysics, v. 59, p. 1.

Shipley, T.H., Houston, M.H., Buffler, R.T., Shaub, F.J., McMillan, K.J., Ladd, J.W., and Worzel, J.L., 1979, Seismic reflection evidence for the widespread occurrence of possible gas hydrate horizons on continental slopes and rises: Am. Assoc. Petroleum Geologists Bull., v. 63, p. 2204.

Shipley, T.H., Buffler, R.T., and Watkins, J.S., 1978, Seismic stratigraphy and geologic history of Blake Plateau and adjacent western Atlantic continental margin: Am. Assoc. Petroleum Geologists Bull., v. 62, p. 792.

Smith, B.N., and Epstein, S., 1971, Two categories of C_{13}/C_{12} ratios for higher plants: Plant Physiol., v. 47, p. 380.

Stoll, R.D., 1974, Effects of gas hydrates in sediments, in Kaplan, I.R., ed., Natural gases in marine sediments: New York, Plenum Press, p. 235.

Stoll, R.D., and Bryan, G.M., 1979, Physical properties of sediments containing gas hydrates: Jour. Geophys. Research, v. 84, p. 1629.

Stoll, R.D., Ewing, J.I., and Bryan, G.H., 1971, Anomalous wave velocities in sediments containing gas hydrates: Jour. Geophys. Research, v. 76, p. 2090.

Swallow, J.C., and Worthington, L.V., 1961, An observation of a deep counter-current in the western North Atlantic: Deep Sea Research, v. 8, p. 1.

Tucholke, B.E., Bryan, G.M., and Ewing, J.I., 1977, Gas hydrate horizons detected in seismic-profiler data from the western North Atlantic: Am. Assoc. Petroleum Geologists Bull., v. 61, p. 698.

Uchupi, E., 1967, The continental margin south of Cape Hatteras, North Carolina: Shallow structure: Southeast Geol., v. 8, p. 155.

Uchupi, E., 1968, Atlantic continental shelf and slope of the United States - Physiography: U.S. Geol. Survey Prof. Paper 529-C, 30 p.

Vail, P.R., Mitchum, R.M., Jr., Shipley, T.H., and Buffler, R.T., 1980, Unconformities of the North Atlantic: Royal Soc. of London, Philosophical Trans., Series A, v. 294, p. 131.

Vail, P.R., Mitchum, R.M., Jr., and Thompson, S. III, 1979, Global cycles of relative changes in sea level, in Payton, C.E., ed., Seismic stratigraphy - applications to hydrocarbons exploration: Am. Assoc. Petroleum Geologists Mem. 26, p. 83.

Villard, P., 1888, On some new gas hydrates (in French: Sur de nouveaux hydrates de gaz): l'Academie des Sciences, comptes rendus, v. 106, p. 1602.

Volkmann, G.H., 1963, Deep current observations in the western North Atlantic: Deep Sea Research, v. 10, p. 493.

Wilcox, W.I., Carson, D.B., and Katz, D.L., 1941, Natural gas hydrates: Industrial and Engineering Chemistry, v. 33, p. 162.

APPENDIX, Confirmed or Inferred Gas Hydrate Locations, is located in the pocket at the end of the report.